PREMIXED COMBUSTION IN A LIGHT DUTY COMPRESSION IGNITION ENGINE THROUGH FUEL AND INJECTION SYSTEM DESIGN: AN EXPERIMENTAL APPROACH

by

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Abstract

Premixed combustion modes in compression ignition engines are studied as a promising solution to meet fuel economy and increasingly stringent emissions regulations. Nevertheless, PCCI combustion systems are not yet consolidated enough for practical applications due to their high complexity in terms of air-fuel charge preparation, combustion process control or due to the difficulties to extent the operating range.

In this framework, this research is aimed to further investigation in the field of PCCI in order to provide additional information, from the fuel side and engine side, for an adequate comprehension of the phenomena and for practical applications.

From the fuel side, this work focuses on providing an overview of the low cetane number (CN) oxy-fuel capabilities to improve both diesel and PCCI combustion in a research light-duty diesel engine. The effects of the cyclohexanone (chosen as representative of the low CN oxy-fuels) and diesel blends on the engine combustion are assessed, i.e. in terms of speed and load range and using PCCI and conventional engine control strategies (EGR, injection pressures, splitted injection, etc.). The results show that low CN oxy-fuels could act as enablers for PCCI combustion, outlining that the low CN and the oxygen content works together to control the smoke emissions. Moreover, the cyclohexanone can be produced from lignin and thus has the potential to be renewable.

From the engine side, the study is aimed to investigate the effect of a specially designed port fuel injection (PFI) system on performance and emissions using n-heptane, as representative of diesel fuel for direct injection, and n-heptane or ethanol as PFI fuel. The results highlight that ethanol (as a low CN fuel) exhibits improved performance in terms of premixed charge formation, combustion control and smoke emissions without evident reduction in fuel efficiency.

To my family

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List of Abbreviations

AIT	Auto-ignition temperature
aTDC	After top dead center
bTDC	Before top dead center
CI	Compression ignition
CH_4	Methane
C_3H_8	Propane
CI	Compression ignition engine
CO	Carbon oxide
CO_2	Carbon dioxide
CR	Compression ratio
CYCLOX	Cyclohexanone
DI	Direct injection
DME	Dimethyl ether
DOC	Catalytic oxidation device
DPF	Diesel particulate filter
EC	Energizing current
EGR	Exhaust gas recirculation
EOI	End of injection
EU	European Union
FAME	Fatty acid methyl ester
GHG	Greenhouse gases
GTL	Gas to liquid
H_2	Hydrogen
HCCI	Homogeneous charge compression ignition
HHR	High heat release
HP	High pressure
HR	Heat release
HTO	High temperature oxidation
ICE	Internal combustion engine
ID	Ignition delay
LD	Light duty
LHR	Low heat release
LNG	Liquefied natural gas
LTC	Low temperature combustion
LTO	Low temperature oxidation
MBF	Mass burned fraction
Mtoe	Million tonnes oil equivalent
NO_x	Nitrogen oxides
NTC	Negative temperature coefficient
ON	Octane number
PCCI	Premixed charge compression ignition
PFI	Port fuel injection
ppm:	part per million
PM:	Particulate matter
PN:	Particulate number
RME:	Rapeseed methyl ester
RoHR:	Rate of heat release
SCR:	Selective catalytic reduction
SI:	Spark ignition
SME	Soybean methyl ester
SOC	Start of combustion
VOC	Volatile organic compound

1 INTRODUCTION

Driven by a need for energy independence and concerns about environmental quality and GHG (Greenhouse gases) emissions [1], the development of new fuels and technologies for the transportation sector is moving forward increased fuel efficiencies [2] and reduced pollutant emissions, using also alternatives and renewable fuels.
In the next two decades, scenarios foresee new vehicles fleet with much more fuel-efficient powertrains, engines powered with renewable fuels, turbocharged downsized engines, hybrid electric drives (plug-in electric vehicles, range extender vehicles, etc.).

This dissertation would like to fit in this context without the presumption to indicate the way forward but the main scope is to give more knowledge in the field of the alternative fuel-efficient and low emission combustions, in particular in the field of PCCI combustion (Premixed charge compression ignition). It would try to elucidate, to some extent, how the covered topics could be a potential ways, or not, to achieve the imposed objectives in terms of fuel efficiencies and pollutant emissions that seem to be conflicting.

There are several ways to meet the prefixed objectives but the solution cannot be "unique" in presence of trade-offs between two or more conflicting objectives. This is the case of many engineering problems where many conflicting objectives have to be satisfied leading to an optimized solution rather than to the best solution.

Moreover, it would also give an overview on the emerging technologies and on the "specially designed" fuels.

[1] The GHG emissions are mainly due to the carbon dioxide(CO_2), methane(CH_4), nitrous oxide(N_2O) and fluorinated gases. These gases have the ability to trap the heat in the atmosphere that lead to the notorious global warming effect and to the climate change.
[2] The fuel efficiency can be interpreted in terms of carbon dioxide production; the higher the fuel efficiency the lower the CO_2 production.

In summary, Chapter 1 attempts to evidence and collocate the importance of the experimental research done in the field of the internal combustion engines. Chapter 2 deals with the technologies and methodologies in the field of advanced and alternative combustions, whereas chapter 3 describes the experimental setup and Chapters 4 and 5 the test result and discussion of tests done. Finally, chapter 6 presents the main conclusions of the experiments and the future work that is going to realize.

1.1 Emissions, legislation and future of the internal combustion engines

In the last century, the internal combustion engine (ICE) has played a key role as power-unit in different sectors of power generation, like transportation sector, energy production, work machines and other niche areas because it has represented the most cost efficient power-unit. For this reason, in the road transportation sector, the number of vehicles in the last decades has grown exponentially representing one of the main actors in terms of petroleum consumption, pollutant and Greenhouse gas (GHG) emissions.
Accordingly, the standard vehicle exhaust emissions regulations has imposed very stringent limits in terms of pollutant and GHG emissions requiring significant changes of the future vehicle characteristics.

1.1.1 Greenhouse gas emissions

Concerning the GHG emissions, the European Commission has developed a mandatory CO_2 (Carbon dioxide) [3] emission target for new passenger cars [4] adopted on 2009 [regulation 443/2009/EC]. The regulation established a fleet-average CO_2 emission target of 130 g/km by each vehicle manufacturer by 2015 using vehicle technology. Moreover, a further emission reduction of 10 g/km is provided by additional measures, such as the use of biofuels. The regulation also defines a long-term target of 95 g CO_2/km that has to be reached in 2020 [1].

[3] The CO_2 represent the majority of the GHG emissions emitted by the internal combustion engines. The natural gas powered engines emit also CH_4(methane) that is a GHG.
[4] There is also a CO_2 target for light duty commercial vehicles that have to be reached from 2016[1].

In order to give an idea about the contribution of the transport sector to GHG emissions and energy consumption of the transport sector it might be interesting to give a look on the next graphs.

The European transportation sector is responsible for about the 32% (Figure 1.1) compared to the total energy consumption and the 20% of total greenhouse gas emissions in 2008 (Figure 1.2) [2].

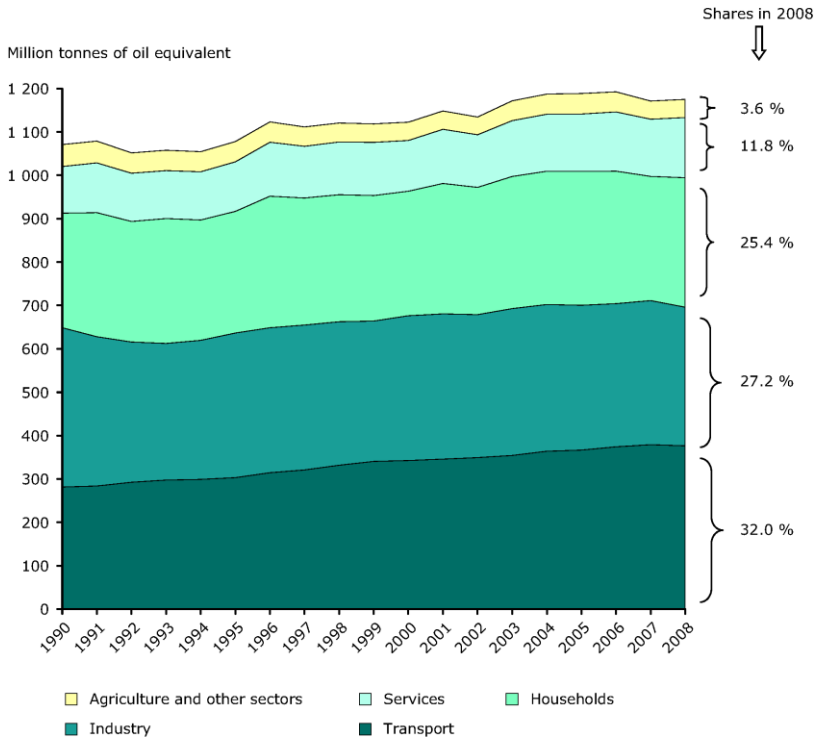


Figure 1.1: Final energy consumptions by sectors (Mtoe), 1990-2008 [2].

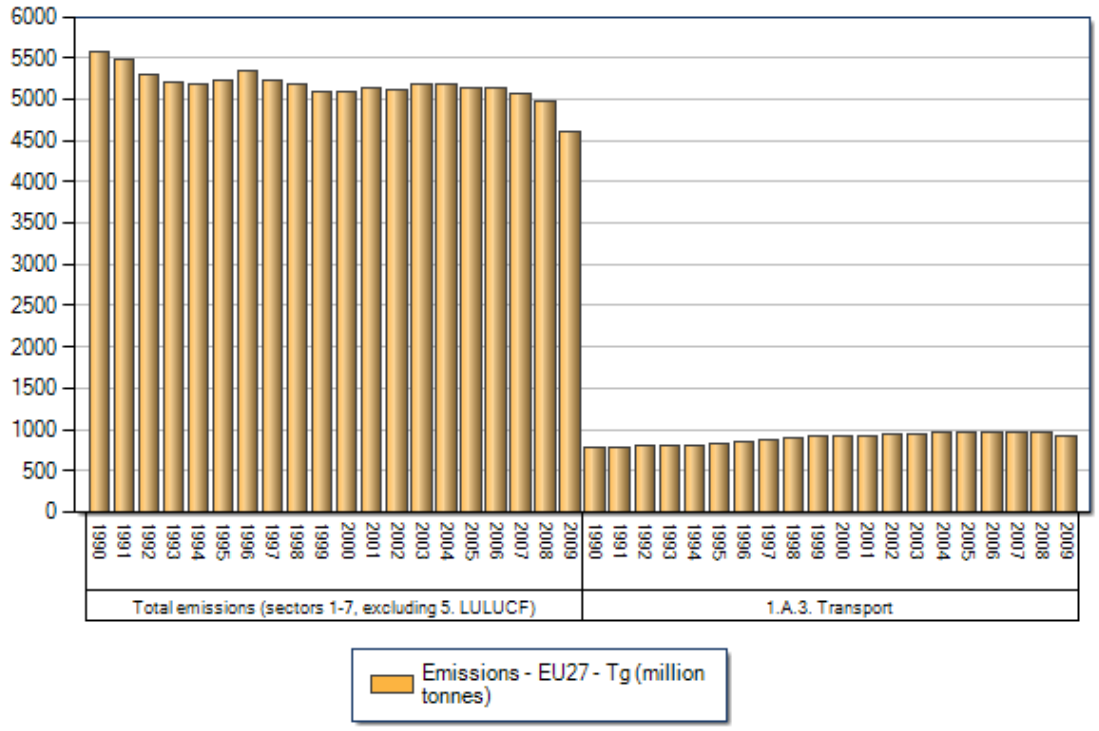


Figure 1.2: Greenhouse gas emissions (CO2 equivalent). Total emissions vs. transport sector emissions in the last two decades [2].

Moreover, the road transportation represents, alone, more than 90% of the total GHG emissions in relation to the whole transportation sector. The light-duty passenger vehicles are the majority of this share therefore, they represent a key segment to target reductions.

More in detail, in Figure 1.3 shows the total and transportation sector change of the European GHG emissions of year 2009 respect to the base year 1990. The total GHG emissions have been reduced whereas the emissions of the transportation sector emissions have been increased, in particular those of the road transportation [2].

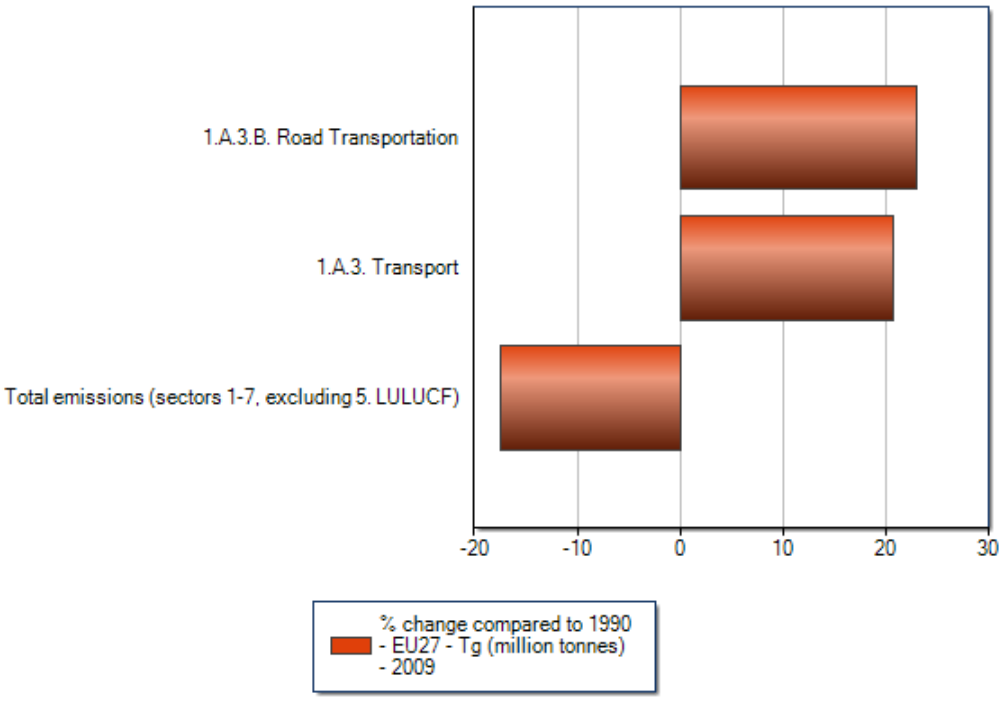


Figure 1.3: Change of GHG emissions, total vs. transport sector and road transportation [2].

In order to invert this trend and to meet the further emission limits, there have been proposed various possible strategies to reduce the road transportation impact such as (i) reducing the carbon content of transportation fuels; (ii) improving the on-road fuel efficiency of vehicles (iii) reducing passenger vehicle travel and (iv) improving traffic flow and operation.

In this context, Cheah *et al.* [3] explored the magnitude, combinations and timings of changes of the vehicles in order to meet the new emission standards. They elaborate four different scenarios in terms of fuel saving[5] technologies and approaches to improving vehicle fuel economy up to year 2030. In particular, the first three scenarios employ different strategies like (a) vehicle light weighting, (b) vehicle downsizing, (c) alternative powertrains whereas the last employ (d) a combination of the previous approaches in the case each of them should be not sufficient to meet the emission and fuel economy standards.

[5] Fuel saving means reduction of CO_2 emissions

One of the results of this study is reported in Figure 1.4. The graph shows the trends of the fuel consumption reduction improving all the vehicle technologies (at constant vehicle size and performance attributes) up to year 2030. At the same time, it is possible to note the fuel consumption improvement changing only the power unit technology.

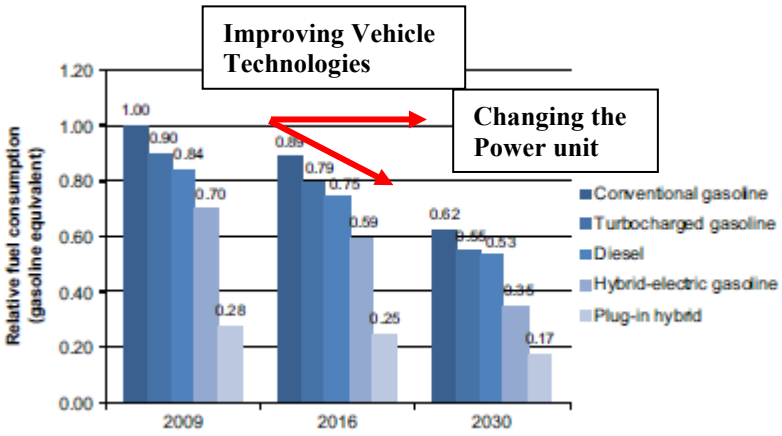


Figure 1.4: Fuel consumption reduction improving the vehicle technologies at constant vehicle size and performance and for the different power units [3].

1.1.2 Emissions

Concerning the harmful engine emissions of the compression ignition engines (CI), this subsection contains an overview of the classification, the limitations and the factors that mostly affect their production.

In general, the term "engine emissions" refers primarily to pollutants in the exhaust [11]. The internal combustion (IC) engines convert chemical energy contained within the fuel into mechanical power. The fuel is made by various hydrocarbons that in a theoretical complete combustion will produce carbon dioxide (CO_2) and water (H_2O) vapour. These gases are not harmful for health, but as described before, CO_2 is considered a greenhouse gas. These ideal combustion gases and any unused air make up the bulk of the exhaust from a real IC combustion engine. Whereas, if occurs a non-ideal combustion process there are formed other emissions, some of which are toxic or harmful for the human health. These can derive from incomplete combustion of the fuel, combustion of lubricating oil, combustion of additives and non-hydrocarbon compounds such as sulphur (from fuel or lube oil), or indeed separate reactions or decompositions of the mixture components at high pressure/temperature.

Thus, for CI engines, there are many factors that affect the emission and these include the preparation of the mixture during ignition delay, the quality of the fuel, the air/fuel mixing process, the residence time of the fuel at different combustion temperatures and the combustion duration in the expansion stroke. Many inherent design features of the engine can also play a role in emissions formation

Currently the *regulated* emission are:

- *Nitrogen oxides (NOx)*
- *Particulate matter (PM)*
- *Hydrocarbons (HC)*
- *Carbon monoxide (CO)*

excluding the further but imminent limits in terms of CO_2 and carbonaceous nanoparticles.

Restricting the field to light duty vehicles, Figure 1.5 reports the EU (European Union) emission limits of diesel and gasoline engines up to the new standards Euro VI [1]. The next Euro VI limits are very stringent for both engines, mainly in terms of NOx (Nitrogen oxide) and PM (Particulate matter) emissions. Moreover, it should be also considered that since Euro 5 there is an additional PM requirement, for a PM total number (PN) limit at 6×10^{11} #/km. This is because, many of researches are going on in order to evaluate and improve the effectiveness of the current after-treatments devices, such as DPF, to retain the particles[6].

[6] It is proved the carcinogenicity of the nanoparticles. The very small dimensions (nm) allow their to penetrate deep into the lung air sacs.

Stage	Date	CO	HC	HC+NOx	NOx	PM	PN
		g/km					#/km
Compression Ignition (Diesel)							
Euro 1†	1992.07	2.72 (3.16)	–	0.97 (1.13)	–	0.14 (0.18)	–
Euro 2, IDI	1996.01	1.0	–	0.7	–	0.08	–
Euro 2, DI	1996.01[a]	1.0	–	0.9	–	0.10	–
Euro 3	2000.01	0.64	–	0.56	0.50	0.05	–
Euro 4	2005.01	0.50	–	0.30	0.25	0.025	–
Euro 5a	2009.09[b]	0.50	–	0.23	0.18	0.005[f]	–
Euro 5b	2011.09[c]	0.50	–	0.23	0.18	0.005[f]	6.0×10^{11}
Euro 6	2014.09	0.50	–	0.17	0.08	0.005[f]	6.0×10^{11}
Positive Ignition (Gasoline)							
Euro 1†	1992.07	2.72 (3.16)	–	0.97 (1.13)	–	–	–
Euro 2	1996.01	2.2	–	0.5	–	–	–
Euro 3	2000.01	2.30	0.20	–	0.15	–	–
Euro 4	2005.01	1.0	0.10	–	0.08	–	–
Euro 5	2009.09[b]	1.0	0.10[d]	–	0.06	0.005[e,f]	–
Euro 6	2014.09	1.0	0.10[d]	–	0.06	0.005[e,f]	–

* At the Euro 1..4 stages, passenger vehicles > 2,500 kg were type approved as Category N_1 vehicles
† Values in brackets are conformity of production (COP) limits
a – until 1999.09.30 (after that date DI engines must meet the IDI limits)
b – 2011.01 for all models
c – 2013.01 for all models
d – and NMHC = 0.068 g/km
e – applicable only to vehicles using DI engines
f – 0.0045 g/km using the PMP measurement procedure

Figure 1.5: EU Emission Standards for Passenger Cars (Category M_1*) [1].

Nitrogen Oxides (NOx): NOx, in the fields of ICE, refers chiefly to nitric oxide (NO) and nitrogen dioxide (NO_2). In particular, for diesel engines NO represents approximately 90% and NO_2 10% of total NOx created by an ICE. NO_X, together with volatile organic compounds (VOC's) and carbon monoxide (CO), is the main precursor of the formation of photochemical smog. Smog is a term used to describe air pollution that is a result of the interaction of sunlight with certain chemicals in the atmosphere is ozone. While ozone in the stratosphere protects earth from harmful UV radiation, ozone on the ground is hazardous to human health. Ground-level ozone forms when vehicle emissions containing nitrogen oxides (primarily from vehicle exhaust) and volatile organic compounds (from paints, solvents, and fuel evaporation) interact in the presence of sunlight. Therefore, some of the sunniest cities are also some of the most polluted.

The NO_X species also exert a direct toxic effect on human health. NO is regarded as being carcinogenic (like soot), and responsible for acid rain and smog. NO_2 is an irritant gas causing pulmonary edema [2][6][7].

In the internal combustion engine, NO is the predominant oxide of nitrogen produced during the combustion. The main source of NO is the oxidation of atmospheric nitrogen but also the fuel if it contains significant levels of nitrogen. NO is formed in both the flame-front and the post-flame gases. In engines, however, combustion occurs at high pressure so the flame reaction zone is extremely thin (~ 0.1 mm) and residence time within this zone is short. In addition, the cylinder pressure rises during most of the combustion process, so that burned gases produced early in the combustion process compressed to a higher temperature that they reached immediately after combustion. For this reason, the NO formation in the post-flame gases often dominates any flame-front produced NO.

According to literature, three primary sources of NO_X have been identified in the homogeneous combustion processes: ***thermal*** $\boldsymbol{NO_X}$, ***fuel*** $\boldsymbol{NO_X}$ and ***prompt*** $\boldsymbol{NO_X}$ [7].

Thermal NO_X is formed in the post-flame by the oxidation of atmospheric nitrogen at relatively high temperatures (T>1600 °C) in fuel-lean environments in a strongly temperature dependent process (Figure 2.4). Thermal NO_X reactions take place in a few tens of microseconds, and are highly dependent on temperature, residence time and atomic oxygen concentration [7]. The formation of thermal NO_X from molecular nitrogen (and its destruction) is governed by the extended Zel'dovich mechanism:

1. $N_2 + O = NO + N$

2. $N_2 + O_2 = NO + O$

3. $N + OH = NO + H$

The equation 3. was introduced by Lavoie & Blumberg (1973). The major contribute in NO formation are given by the first two equation whereas the last contribute particularly in fuel-rich mixtures. The forward and reverse rate constants for these reactions have been measured in numerous experimental studies; recommended values are reported in Table 1.1 [4].

Reaction	Rate constant [cm^3/(mol s)]	Activation energy	Temperature range [K]
1	**7.6×10^{13} exp(-38000/T)**	**38000**	**2000 - 5000**
reverse 1	**1.6×10^{13}**	**-**	**300 - 5000**
2	**6.4×10^{9} exp(-3150/T)**	**3150**	**300 - 3000**
reverse 2	**1.5 x 109 exp(-19500/T)**	**19500**	**1000 - 3000**
3	**4.1×10^{13}**	**-**	**300 - 2500**
reverse 3	**2×10^{14} exp(-23650/T)**	**23650**	**2200 - 4500**

Table 1.1: Forward and reverse rate constant for NO formation mechanism [4].

Reaction 1. determines the rate of formation due to its high activation energy of breaking the triple bond of molecular nitrogen (N_2), and is temperature-sensitive. The temperature-dependence also results from the temperature sensitivity of the O atom equilibrium concentration [7].
A simplified formula for the initial NO formation rate could be written, as proposed by Heywood [4], as:

$$\frac{d[NO]}{dt} = \frac{c_1}{T^{1}/_{2}} \cdot e^{\left(\frac{-c_2}{T}\right)} \cdot [O2].[N2] \quad [mol/cm3 \cdot s]$$

where [...] denote species concentrations in moles per cubic centimetre and c_1 and c_2 are two positive constants. The forward rate constant for reaction 1. and the reverse constant for reaction 2. and 3. have large activation energies which results in a strong dependence of NO formation rate on temperature. Thus, high temperatures and high oxygen concentrations result in high NO formation rates.

Fuel NO_X refers to NO_X formed by the combustion of fuels containing organic nitrogen in the fuel; dependent on local combustion conditions and nitrogen content in the fuel. It is usually assumed that fuel NO_X is a source of nitrogen oxides via formation of precursors (NH_3, HCN, and CN). In fuel-rich regions, these nitrogen-containing species will typically be reduced to N_2, and in fuel-lean regions, they are generally oxidized to form NO. The amount of fuel nitrogen converted to NO is sensitive to the air/fuel ratio but only weakly dependent on temperature, in contrast to the strong temperature dependence of NO formed from atmospheric nitrogen [4]. Fuel NO is formed more readily (occurring on a time scale comparable to that of combustion reactions) than thermal NO because the N-H and N-C bonds, which are very common in fuel-

bound nitrogen, are much weaker than the triple bond in molecular nitrogen which must be broken for thermal NO formation. Controlling the local environment in which nitrogen is released from the fuel is a primary means of controlling NO emissions and although the amount of fuel NO in the diesel exhaust is negligible with the diesel fuel used today, its contribution to the total amount of NO_X produced from the engine must be considered [7].

Prompt NOx form in the flame-reaction zone and are produced by the reaction of atmospheric nitrogen with hydrocarbon radicals (C, CH, CH_2, etc.) in fuel-rich regions of flames. This process results in the formation of fixed species of nitrogen (NH, HCN, H_2CN, CN, etc.) which can then oxidized to form NO. Since the prompt NO_X mechanism requires a hydrocarbon to initiate the reaction with nitrogen, this mechanism is much more prevalent in fuel rich than in fuel-lean hydrocarbon flames [7]. Anyway, the contribution of prompt NO_X is normally considered negligible.

In general, terms, the critical equivalence ratio for NO_X formation in high-temperature high-pressure burned gases, typical of DI-diesel engines, is close to stoichiometric. The critical period occurs when burned gas temperatures are at a maximum, i.e., between the start of combustion and shortly after the occurrence of peak cylinder pressure. Mixture which burns early in the combustion process is especially important since it is compressed at higher temperature, thereby increasing the NO formation rate, as combustion proceeds and cylinder pressure increases. After the time of peak pressure, burned gas temperatures decrease as the cylinder gases expand. The decreasing temperature due to expansion and due to mixing of high-temperature gas with air or cooler burned gas freezes the NO chemistry. This second effect means that freezing occurs more rapidly in the diesel than in the spark-ignition engine, and there is much less decomposition of the NO. The parameters that most significantly affect the formation of NOx in diesel engines are the in-cylinder gas temperature, the availability of oxygen, the cylinder pressure, as well as the residence time of the fuel/gas mixture in locations with favourable temperatures and oxygen concentration for the formation of nitric oxides. All these parameters, in turn, depend on the inlet air pressure and temperature, the exhaust gas recirculation (EGR) rate, and on the injection timing with respect to the engine cycle [4].

Particulate Matter (PM) is a mixture of carbonaceous soot, as well as other solid and liquid materials. They are small solid or liquid particles, mostly less than 2.5 microns in size, and consist of a complex mix of engine oils, sulphates and inorganic materials. Different types of particulates are emitted from diesel engines under different modes and operating conditions.
Diesel particulate emissions are increasing and this fact concerns really much because health experts have demonstrated that these particles contribute to a variety of lung-related illnesses including asthma, emphysema and bronchitis. The International Agency for Research on Cancer (IARC) considers particulate matter (PM) a probable human carcinogen. Consequently, the generation of PM is under intense study by researchers from various disciplines.

The Particulate matter can be classified as:

- *Solid Fraction (Solid particulate matter)* consisting of carbonaceous soot and ash (including metallic).
- *Soluble Organic Fraction (Liquid Particulate Matter)* consisting of organic material derived from the fuel (hydrocarbons) and organic material derived from the engine lubricating oil (higher hydrocarbons).
- *Water Particulate* consisting of water and sulphuric acid H_2SO_4 (when fuel sulphur is present).

A typical structure of engine particles [14] is reported in Figure 1.6.

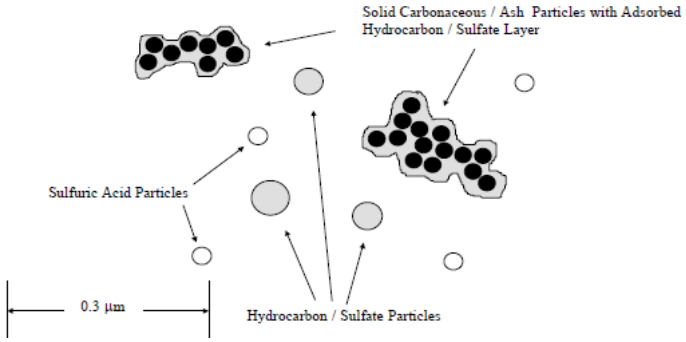


Figure 1.6: Typical structure of engine particle [14].

Soot production process consists of some principal events which main steps are represented in Figure 1.7 [10], and
Figure 1.8 [12].

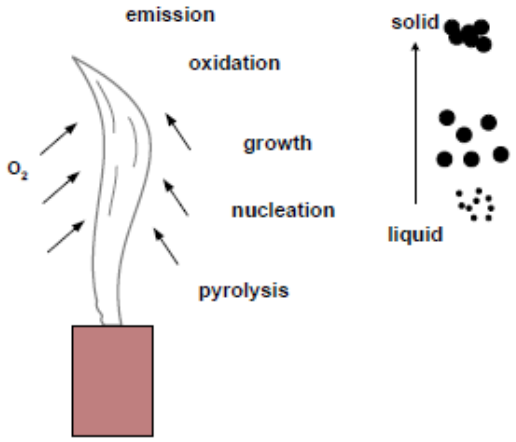


Figure 1.7: Important steps of soot formation in a diffusion flame [10].

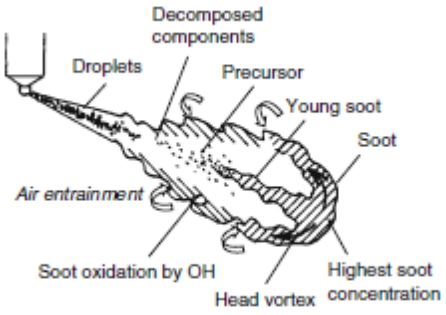


Figure 1.8: Mechanism of soot formation and oxidation in a transient reacting spray [12].

- *Pyrolysis:* formation of soot precursors. Large quantities of reactive molecules are formed, such as acetylene (C_2H_2), phenyl radical (C_6H_6), cyclic structures, etc. by polymerization reactions, these precursors can grow to macromolecules. Due to their high thermal stability, cyclic structures play an important role.

- *Nucleation:* formation of primary particles. As soon as the molecules mentioned above reach a sufficient supersaturation first particles are formed by nucleation. Typical number concentrations of such nucleation particles are in the order of $10^{12}/cm^3$. They have diameters about a few nanometers.

- *Particle growth:* Immediately after nucleation, the particles start to grow. On the one hand, this growth occurs by coagulation, which is very rapid due to the high number concentration of the nucleation particles. Another important process is surface growth. This means growth

by attachment of material from the gas phase. Surface growth determines the total particle mass.

- *Dehydration*: in the last step oxidation processes are dominant so the particle burnout. These reduce the particle mass. The hydrogen content decreases (dehydration). Under certain conditions, the particles can burn completely.

More details about the formation process can be found in [12]. The chemical composition of soot particles depends on the temperature in the engine exhaust and on the particulate sampling system. At high temperatures (>500 °C), its composition is mainly elementary carbon and organic carbon. Below 500 °C, the particles become coated with adsorbed and condensed high molecular weight organic compounds, among which, unburned hydrocarbons, aromatic and oxygenated hydrocarbons and inorganic species such as sulphur dioxide and sulphuric acid (sulphates).
Considering the high complexity of the combustion in compression ignition engines, the dependence between PM emission and the engine's physical parameters is very complex due to the difficulty of isolating the effects of each of them. For example, reasons for incomplete burnout of the particle emission are the local or global lack of oxygen, bad mixing, not enough time for complete combustion (combustion is abruptly terminated when the outlet valve opens), chamber geometry, the intake temperature and pressure, the injection system, etc.. Other details can be found in literature, for example in [4], [26].

Particle number PN: as reported in Figure 1.5, the regulation foresees limits also in terms of PN. There is increasing evidence that several health effects are associated with the ultra-fine particles with diameters below 100 nm. Recent research shows that they can penetrate the cell membranes, enter into the blood and even reach the brain. Some investigations indicate that particles can induce inheritable mutation [13]. The nanoparticles (20-100nm) originate from different source such as organic compound (elemental carbon), deriving from the fuel and oil, or in some case metal oxides and metallic PM. Several fuel and engine oil additives include metallic compounds. This results in some metal oxide and elemental emissions, including metals such as; iron, copper, zinc, cerium, and phosphorus.

Usually, particles are classified according to their diameter in [15]:

- Nano: particles smaller than 50nm;
- Ultrafine: particles with an aerodynamic diameter lower than 0.1μm;
- Fine (PM2.5): particles with an aerodynamic diameter in the size range from 0.1 up to 2.5μm;
- Coarse (PM10): particles with an aerodynamic diameter in the size range from 2.5 up to 10μm;
- Supercoarse: particles with an aerodynamic diameter higher than 10μm.

The particles usually form separated modes in the particle size distribution function (PSDF). Figure 1.9 displays a typical size distribution of atmospheric particulate matter [14]. It possible to distinguish three modes:

- Nuclei mode: particles smaller than 50nm usually formed from volatile precursor during exhaust dilution and cooling processes;
- Accumulation mode: particles from 50nm up to 1000nm size range usually consists of carbonaceous agglomerates and adsorbed material;
- Coarse mode: particles larger than 1000nm consists of reentrained accumulation mode particles, crankcase fumes.

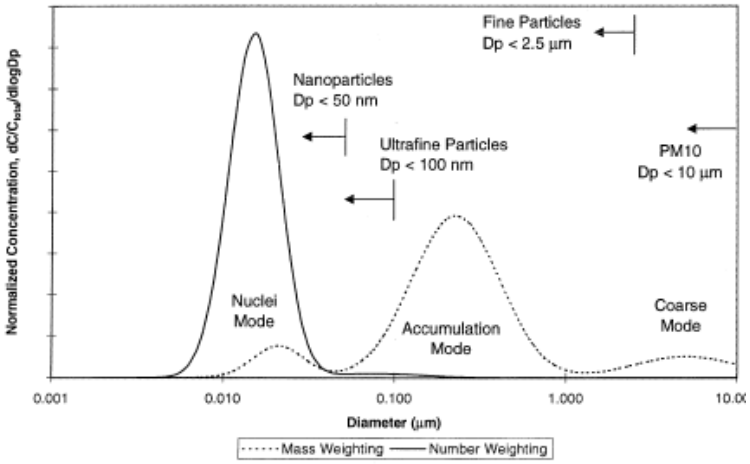


Figure 1.9: Typical size distribution of Diesel particulate matter [14].

The different modes are used to characterize the emission of the nanoparticles in the test results (see Chapters 4 and 5).

Hydrocarbons (HC), in the exhaust of a CI engine, consist of unburnt hydrocarbons (UHC), partially decomposed fuel molecules and recombined intermediate compounds. In direct injection CI engines, hydrocarbons originate predominantly through insufficient mixing of fuel and air, in regions where the flame quenches on the walls and where excessive dilution with air prevents the combustion process from either starting or going to completion.

In particular, during the ignition delay period, the fuel injected mixes with air and can produce a wide range of equivalence ratios. This is because some regions in the combustion chamber are too lean to support combustion, whilst others fall within the flammability limits and finally some regions are too rich and evaporate too slowly to combust also if the global mixture is lean. When the fuel is injected after the start of combustion, in the mixing controlled combustion region, fuel pyrolysis may occur (due to the high temperature and local low oxygen environment into which the fuel is being injected) or, where oxygen is available, there will be a rapid oxidation. Any conditions that slow down the rate of pyrolysis and/or oxidation, may lead to a localised rich mixture and therefore, a delay or lack of combustion. When this happens, the exhaust is likely to contain more UHC [11].

Moreover, fuel that vaporizes from the nozzle sac volume during diffusive combustion phase, liquid films on combustion chamber surfaces, quenching in the squish volume outside the piston bowl, are also a source of HC. A small portion of these hydrocarbons originate from the lubricating oil left in a thin film on the cylinder wall, piston and perhaps on the cylinder head. These oil layers can absorb and desorb fuel hydrocarbon components, before and after combustion, respectively, thus permitting a fraction of the fuel to escape the primary combustion process unburned.

The mechanisms of formation and oxidation of the hydrocarbon molecules depend upon most of the engine operating variables, i.e., fuel-air ratio, injection time, swirl and of course injection system design, time and rate of injection.

Carbon Monoxide (CO) is a product of incomplete combustion, formed when hydrocarbon species are not completely oxidised to carbon dioxide. It is a colourless and odourless gas, highly toxic to human beings and other life forms. There are several potential sources of CO emissions

which include over-lean mixture regions, in the temperature range 800<T<1400K, that burn slowly and over-rich regions that have insufficient oxygen availability for complete combustion but temperatures enough high to oxidise the source fuel.
In hydrocarbon flames, the dominant reactions for oxidation of carbon monoxide are [9]:

1. $CO + OH = CO_2 + H$
2. $CO + HO_2 = CO_2 + OH$
3. $CO + O_2 = CO_2 + O$

More importantly in the oxidation of CO is the amount of OH present. OH radical concentration increases exponentially with peak charge temperature. The oxidation of CO is dominated by the reaction described in Equation 1, such as the oxidation process is highly sensitive to temperature. A minimum temperature of ~1500 K has to be finding because it is necessary for near complete CO oxidation. As with HCs, the original fuel compound does not affect the final oxidation process even if the required local equivalence ratio varies in accordance with fuel in order to attain the required threshold temperature. Complete oxidation of HCs occurs at lower temperature than that of CO, allowing CO to remain in an unoxidised state, leading to higher CO than HC emissions.
In general, Diesel CO emissions are low because the mixture is globally lean. Nevertheless, since this mixture is highly heterogeneous a certain amount of CO is generated locally in the combustion chamber. In the case of combustions of high-diluted charges (e.g. high levels of EGR), the CO increase due to the over lean zones as well low combustion temperatures inside the chamber. More details regarding this aspect, in particular for new/alternative combustions, are reported in the next Chapters.

1.1.3 Unregulated Emissions

Even if the unregulated emissions go beyond the objective of this thesis, it is worth to spend some words on the unregulated emissions that have been found in CI engine exhaust. Although they are at much lower concentration levels than the regulated emissions, they could be potential

future regulated compounds. Some of them represent a part of the complex PM emission whereas others are gas phase species:

- *Polycyclic aromatic hydrocarbons (PAHs)* are atmospheric pollutants that consist of fused aromatic rings. Some PAH compounds have been identified as carcinogenic.
- *Nitrous oxide, N_2O (not included in NOx measurements)* is a possible future concern as it is promoted in some aftertreatment systems for use as an oxidant. As a pollutant, it is a powerful greenhouse gas at 298 times the effect of CO_2.
- *Aldehydes* are a part of the gaseous emission from CI engines Aldehydes are the product of partial oxidation of hydrocarbons. They mainly consist of acetaldehyde (CH_3CHO) and formaldehyde (CH_2O) that have proved to produce health effects and be probable carcinogens. As occurs for hydrocarbon formation, aldehydes originate in a region where the flame extinguishes. Aldehydes are highly oxygen concentration-dependent thus, the use of alcohol fuels in diesel engines substantially increases aldehyde emissions principally if they are used in quantities comparable to gasoline and diesel.
- *Sulphur dioxide (SO_2),* from sulphur present in the fuel and the lube oil. Actually the sulphur level in the fuels are quite low (<10ppm), but higher levels may still exist in some developing markets. Sulphur dioxide is a precursor of acid rain and atmospheric particulate. Automotive catalysts can be rendered ineffective (poisoned) by sulphur, as it deactivates the catalytic sites of the catalyst.
- *Nitrogen dioxide, (NO_2)*, constitutes a part of the NOx emission (it is more toxic than NO, the other component of NOx) it could be anticipated that in the future NO_2 may be regulated individually.
- *Dioxins (polychlorinated dibenzodioxins)*, have lipophilic (dissolve in fats) properties, and are known teratogens (cause birth defects), mutagens, and suspected human carcinogens. Dioxin emissions are a problem only when chlorine is present during combustion. Consequently, chlorine levels in diesel are now strictly controlled. Potentially biodiesels can contain small levels of chlorine, if certain herbicides are used in production and this must be avoided.

1.1.4 The future of the internal combustion engine

The internal combustion engine (ICE) will continue to improve and remain the dominant technology for the next two or so decades, although we are likely to see an increase in powertrain electrification [5]. Moreover, the need to improve the fuel economy and to reduce the pollutant emissions of the ICE is driving to continuous improvements in all the conventional internal combustion engines. These improvements are considered capable of bringing to a reduction of about 30% to 40% in fuel consumption of light-duty vehicles over the next two 20 years (see Figure 1.5) [3].

Such improvements could be achieved through the developments of breakthrough technologies, such as two-stage turbochargers, electronic engine control, direct injection (DI) system (gasoline engines), High pressure Common rail (HP-CR) injection systems, Exhaust gas recirculation (EGR), Diesel oxidation catalyst (DOC), Diesel particulate filter (DPF), selective catalytic reduction (SCR), etc.

In this framework, due to combination of energy efficiency, power, reliability and durability, the diesel engines have many advantages. There are, however, several challenges still have to be overcome. In fact, one of the biggest drawbacks of diesel engines is the so-called diesel dilemma. This refers to the trade-off between NOx and PM, i.e. when attempting to reduce NOx by reducing the combustion temperature, PM emissions increase (e.g. due to poorer oxidation) and vice versa. Therefore, a lot of research is being conducted into the field of new combustion concepts in order resolve this problem [18].

The reason why it is so difficult to control NOx and PM emissions in Diesel engines is related to the basics of the conventional Diesel combustion process. The air-fuel mixture is globally lean but not homogeneous, with local conditions in the combustion bowl of very high temperature and oxygen concentration, ideal for NOx generation [25]. The local rich mixture conditions together with high temperatures (T~1800K) promote moreover soot formation. Therefore, the NOx and the soot emissions are inversely linked in the conventional diesel combustion.

To overcome to this dilemma, the combustion process must be modified to achieve more homogeneous charge, the so-called advanced combustions, in order to reduce the mean charge temperature and without unacceptable deterioration of efficiency and combustion noise [25]. More details about new and alternatives combustions are reported in the next Chapter 2

With the introduction of the actual Euro 5 emission standard to meet the targets in terms of particulate emissions (see Figure 1.5), most of Diesel engines has been equipped with an HP CR fuel injection system and with DPF, whereas to meet the targets in terms of NOx, high levels of EGR has been used. However, the combination of these technologies could be not sufficient to close the gap to further Euro6 standards.

In this field, researches are going on in order to develop advanced engine control units and strategies such as the "torque controlled" diesel engine control method [19]. This methodology, called Closed-Loop Combustion Control (CLCC), is able to detect and control in real time the level of biodiesel blend and the combustion respectively. The latter, in combination with the actual engine technologies should lead to flex-fuel engines. The flex-fuel engines permit the use of alternatives/renewable and low emission fuels, at constant performances and let to meet the further targets in terms of pollutant and GHG emissions.

Thus, since further improved combustion process such as advanced diesel combustion (HCCI, PCCI, LTC. etc.) have only reached research status up to now, EURO 5/EURO 6 level will necessitate for aftertreatment technologies such as DPF, DOC or DeNOx, etc.

Anyway, in order to improve the global engine efficiency, necessary more attention has to be devoted to the improvement of the new combustion concepts, which are able to reduce the emissions maintaining high the efficiency. This permits simultaneously to reduce the load devolved to the aftertreatment system and increase the global engine fuel efficiency.

1.2 Compression ignition fuels

The dilemma of matching engines and fuels with each other is being raised. In other words, the question such as, how far should the engines be optimized for the use of a specific fuel, or vice versa, how far should a fuel's composition be optimized for use with a specific engine technology, have to be assessed. This is why, this paragraph will focus essentially on the fuels characteristics assessing, to some extent, their impact on the CI engines.

Concerning the GHG and pollutant emissions, significant changes in the mix of transportation fuels in the future are expected. Moreover, there are also other factors driving such changes for instance, the rate of introduction of new automotive technologies, the price of petroleum and

petroleum products, the rate of utilization of resources from agricultural and forestry sectors, the availability of new sources such as natural gas, etc.

Hence, all these aspects are leading to a deeper investigation concerning the creation of many new potential fuels. Obviously, their practicability must be assessed in terms of a wide range of physical-chemical properties, in relation to the operational condition in different engines. Intrinsic fuel properties include volumetric energy, vapour pressure, heat of reaction, latent enthalpy of vaporization, *etc.* Other important combustion properties include the minimum ignition energy, laminar burning velocity, turbulent flame burning and quenching, auto-ignition delay time, octane numbers (RON, MON), cetane number (CN) and so on.

In the follow are reported only the most common parameters, which regulate and characterize the compression ignition fuels:

- *Cetane number (CN)*[7]*:* represent the ignition quality of CI fuels [24]. The higher the cetane number, the greater the fuel's tendency to ignite. A high CN corresponds to a short ignition delay, whereas a low CN increase the ignition delay and then the mixing time between air and fuel leading to undesired spike in the first part of the heat release and accordingly in the pressure trace. Higher spikes determine also higher combustion noise and relatively higher amounts of NO_X. The average values for conventional diesel fuels are between 40 and 60.
- *Auto-ignition temperature (AIT):* there are several ways to define the auto-ignition temperature of the fuel, which depends not only on the chemical composition but also on many other parameters that define the physical condition of the system where the mixture air/fuel will burn (i.e. fuel fraction in the mixture, pressure, heat conductivity, etc.). A simple way to define the AIT is the lowest temperature at which the fuel mixture with air will spontaneously ignite in a normal atmosphere without an external source of ignition. In the case of the internal combustion engine (ICE), this occurs when the energy released by the low temperature reactions (radical formation) during the compression stroke is larger than the heat loss by the surrounding walls of the combustion chamber. A higher AIT reduce the tendency of knock in the spark ignition (SI) engines whereas in the non-conventional combustions like HCCI/PCCI ample the time for the mixing process between fuel and air.

[7] The CN of a diesel fuel is defined in a standard CFR single cylinder test engine with variable compression pistons

- *Volatility/boiling curve:* volatility may be specified by the boiling curve and represents the distillation temperatures, which various percentages of the original sample have evaporated. Higher volatility fuels will be characterized by lower temperatures for given fixed percentages of evaporated sample, or conversely, by higher percentages evaporated at or below a given temperature. A low initial boiling point makes a fuel suitable for use in cold weather, but also means a lower CN and poor lubricant properties raising the wear risk [24]. It is important to highlight that sometimes the fuels (diesel, gasoline) are blend of hydrocarbons, therefore there can be define a distillation curve. In the case of pure fuel, the curve is reduced to a boiling point.
- *Lubricity:* is a measure of the fuel capacity to reduce the friction between mechanical parts. The lubricity is measured in a High Frequency Reciprocating Rig method (HFRR) that measure the amount of wear WSD (Wear scare diameter) in μm. Diesel must have WSD ≤ 460 μm reached with the use of lubricity enhancers since the introduction of desulfurized diesel fuels with lower lubricating characteristics.
- *Low heating value (LHV):* is usually specified to express the energy content of the fuels. The HHV (High heating value) is higher than the LHV since it includes the heat trapped in the water vapour (latent heat). The LHV of diesel fuel is about 42.5 MJ/kg. Oxygenates fuels such as alcohol, FAME (Fatty acid methyl esters), etc., have a lower calorific value than pure hydrocarbons because the oxygen bonded in them does not contribute to the combustion process.
- *Density:* the energy content of fuels per unit of volume increases with density. The use of fuels with widely different densities causes variations in mixture ratios due to fluctuations in calorific value.
- *Viscosity:* is a measure of the fuel resistance to flow due to internal friction. Viscosity is measured with various types of viscometers and rheometers. The kinematic viscosity[8] is measured in mm^2/s and is comprised between 2 and 4.5[9] for diesel fuel. Leakage losses in the fuel injection pump could result if diesel fuel viscosity is too low; high viscosity (e.g. biodiesel) also changes the spray pattern due to the formation of larger droplets. Indeed, viscosity is the most important parameter affecting spray atomization process [24].

[8] The kinematic viscosity is the *dynamic viscosity* divided by the density(typical units mm^2/s, Stokes, St)
[9]The European Standard EN 590 define the requirements of diesel fuel

In the next subsections are itemized the most common conventional and alternatives fuels considered as diesel-like fuel for the compression ignition engines. A table of the main fuel characteristics used during the research is reported in Table 6.1.

Petroleum fuel

Diesel fuels are the product of graduated distillation of crude oil. They contain a whole range of individual hydrocarbons with boiling points ranging from roughly 180°C to 370°C. Diesel fuel ignites (AIT) on average at approximately 350°C which is very early in comparison with gasoline (on average 500°C). Traditional, petroleum-based diesel fuel is still expected to represent the majority of CI fuels during the next 15 years and its composition will probably not change even if the new regulation foresees an increasing percentage (5-10%) of biodiesel in blend with diesel. Sulphur is a major source of particulate and acidic emissions but on-road sulphur levels in fuel have declined dramatically in recent years. In Europe, the current sulphur specification for diesel is 10 ppm. These reductions have reduced PM emissions, and enabled the introduction of catalytic after-treatment systems in light and heavy-duty diesels. However, the lack of availability of low-sulphur diesel is a major barrier to the wide scale deployment of diesel emission control devices in developing countries.

Two significant sources of new diesel fuels are the so-called first and second-generation biofuels that are respectively, the fatty acid esters and the F-T fuels (Fischer and Tropsch or synthetic diesel). In Table 1.2 are reported the main physical and chemical fuel characteristics of these alternative fuels. In particular, there are reported the fatty acid methyl esters (FAME), e.g. RME (Rapeseed methyl ester) and SME (Soybean methyl ester) and the F-T fuel, i.e. the GTL (Gas to liquid). Their impact on the combustion, in terms of performance and emissions are widely assessed [20].

Feature	Method	Petroleum diesel	GTL	RME	SME
Density @ 15 °C [kg/m3]	*EN ISO 12185*	840.1	777.5	883	884.4
Viscosity a 40 °C [mm2/s]	*EN ISO 3104*	3.141	2.547	4.254	3.958
Oxidation Thermal Stability a 110°C h	*EN 14112*	-	-	8.6	7.9
Cetane Number	*EN ISO 5165*	51.8	73.9	52.3	48
Low Heating Value [MJ/kg]	*ASTM D3338*	43.1	43.53	37.35	37.25
Distillation [°C]	*IBP*		203.1	322	320
°C	*10% vol.*		230.3	333.2	332.1
°C	*50% vol.*	280.1	265.9	337	335
°C	*90% vol.*	338.1	305.8	343.3	341.2
°C	*95% vol.*		312.2	347	345.6
°C	*FBP*	362	317.3	360	362
Carbon [%, m/m]	*5991*	86.5	84.3	78.5	78.4
Hydrogen [%, m/m]	*5991*	13.5	14.4	10.8	11.0
Nitrogen [%, m/m]	*5991*	-	1.3	0.2	0.2
Oxygen [%, m/m]	*5991*	-	0.0	10.5	10.4
Polyaromatic content	*wt.-%*	~4	0	0	0

Table 1.2: Main fuel parameters

Biodiesel (First generation biodiesel)

Biodiesel refers to esters of fatty acids. These are usually fatty acid methyl esters (FAME), but may also be ethyl esters. The primary source is plant oils such as soy, palm, rapeseed, and jatropha and consists primarily of triglycerides.

First generation biodiesel are produced through a trans-esterification process with alcohol (Figure 1.10) that features both high energy conversion efficiency and fuel yield from processed oil, these two characteristics are the main responsible for the overall GHG emissions benefit of biodiesel in WTW (Well to wheel) analyses [23].

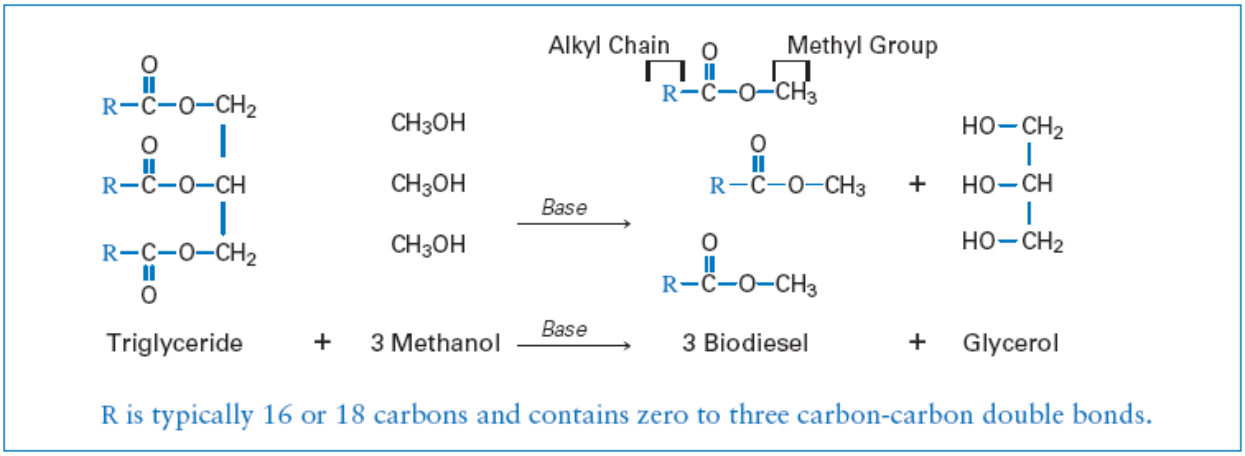


Figure 1.10: Trans-esterification of vegetable oil to biodiesel

When purified, the resulting product contains oxygenated molecules that have a relatively narrow molecular weight distribution in the diesel fuel range.

The methanol used for trans-esterification is generally produced from natural gas or coal, and is thus not obtained from biologic sources. Relative to petroleum-based diesel fuel, fatty acid methyl esters have a number of benefits and challenges, which are summarized in Table 1.3.

Advantages of Biodiesel	*Disadvantages of Biodiesel*
Lower emissions of PM, HC, CO, PAH	*Slightly higher emissions of NOx and possibly aldehydes*
Near zero sulphur content	*Higher viscosity*
Lower aromatic content	*Poorer low-temperature*
Better lubricity	*Poorer oxidative stability*
Higher Cetane Number	*Lower energy content*
Lower GHG(life cycle basis)	*Increased engine deposits*

Table 1.3: Comparison of biodiesel with petroleum Diesel; Properties and performance.

Negative aspects of biodiesel performance can be overcome through blending or using additives or both. While it may be used neat, biodiesel is most commonly used as a blendstock. ASTM International has developed a specification for pure biodiesel (2010a), and 5% (volume) biodiesel

(B5) is approved for use under the diesel specification (D975). ASTM has developed a specification for higher concentrations, B6-B20 (ASTM 2010b). Use of biodiesel is expected to grow in the outlook period.

The emission effects of biodiesel have been largely studied and analysed [20].The data show that biodiesel reduces emissions of PM, hydrocarbons, and CO and somewhat increases emissions of NOx. Moreover, the oxygen content of the FAME is significant, exceeding 10% of the total mass, and is responsible of the fuel LHV reduction of the same magnitude.

Because conventional diesel fuel is highly paraffinic and biodiesel fuels contain esters, it is possible that unregulated emissions will be affected. Based on the particular vegetation source used to produce the biodiesel fuel, emissions of formaldehyde and acetaldehyde (unregulated emissions) may increase, as compared with a petroleum diesel because of the higher oxygen content of the biodiesel (see paragraph 1.1.3). In fact, respect to the second-generation biofuels, FAME retains trace of original feedstock used for oil production, which has different implications in terms of chemical and physical properties of the biodiesel itself, such as oxidative stability (primarily), lower heating value (LHV), stoichiometric air-to-fuel ratio, viscosity, evaporation curve, etc.

Fischer-Tropsch Diesel (Second-generation biodiesel)

F-T diesels are usually indicated with XTL, where X denotes the specific source feedstock and TL (to Liquid) highlights the final liquid state of the fuel. The input feedstock can be either renewable Biomass (hence BTL) or fossil fuels, as natural Gas (GTL) or Coal (CTL). Looking at the renewable BTL production, it has minor interferences with the human food chain with respect to biodiesel, since non-edible biomasses can be employed or, in case of animal-edible biomasses, the whole plant can be processed, as for the cellulosic ethanol production. The XTL shows, respect to the first generation of biofuels instead much better stability in the chemical composition, which is essentially driven by the synthesis process itself and not by the baseline feedstock, and can therefore be managed in a more consistent way [20].

In fact, if engine manufacturers develop new engine technologies that take advantage of the special properties of F-T diesel, then a separate grade of fuel could be produced converting the process to adapt it to the final product.

F-T diesel producing process is consisting of two steps. First, a feedstock is thermally treated to produce a synthesis gas (syngas) consisting primarily of CO (carbon oxide) and H_2 (hydrogen). In the second step, the synthesis gas is reacted catalytically to produce a mixture of hydrocarbons (long paraffin chains + wax) and then hydrocracked to produce the desired end product (kerosene, diesel, Jet fuel, Naphtha, etc.). The resulting fuel is similar to petroleum diesel (paraffin olefin) in molecular weight range (C8–C24), although the distributions may not match exactly. The F-T diesel fuel is extremely high quality and has low or zero aromatics and sulphur, along with a very high cetane number >70 (see Table 1.2).
One of the most important advantages of the F-T fuels is that they are aromatic free, and as known, the aromatics are soot precursor.

In one study of a light-duty "torque controlled" diesel engine, F-T diesel, in particular GTL has been shown to reduce CO (30%) and HC (50%), at more or less constant NOx and PM emissions, relative to petroleum diesel. This test were performed at constant combustion phasing and IMEP so that the potential advantages, due to the absence of aromatics, in terms of PM reduction are overcame by the higher CN that lead to a more diffusive combustion [20].

Alcohols and Ethers

Alcohols and ethers have been proposed for use either in diesel engines, neat or in mixtures with diesel fuel. Alcohols such as methanol and ethanol are not particularly miscible with diesel fuel and their use is under studying.
Within the outlook period of the next decade, ethers such as dimethyl ether (DME) can be good diesel fuels. DME is also highly volatile and flammable; its physical properties are similar to C_3H_8 (propane). Its widespread use in transportation would require expansion of the LPG infrastructure to transport and store it. There is interest in DME use in Asia and some plants are being built in China and Japan. Coal and natural gas are the primary feedstocks for DME production. However, the most interesting takes into consideration that DME can also be produced from the thermochemical conversion of biomass to produce synthesis gas, which is then followed by the catalytic conversion of the synthesis gas to DME. Unlike any other synthetic diesel fuel, DME virtually eliminates soot emissions and the need for DPFs [20].

Innovative - renewable fuel

To be acceptable, biofuel feedstocks must be sustainably produced in terms of agricultural practices, forest management, protection of bio-diverse ecosystems, etc. 2th generation biofuels do not compete with food and fibre and therefore, ligno-cellulosic, forest and agricultural residuals, are promising alternatives in terms of renewable and alternative fuels production.

Besides, for the production of the already mentioned renewable fuels, such as Biodiesel, BTL, and DME, new biomass feedstocks are being considered, e.g. example fatty acids from algae farming. Or else, glycerine as a significant by-product of biodiesel production. In this field, research is underway to find new uses for this product evaluating the possibility to use this by-product as a fuel in blend with petroleum diesel fuel.

Other innovative fuels are cyclic oxygenates fuels (used in this research). They can be produced from biological feedstock, more specifically, from lingo-cellulosic biomass (also known as plant waste/residue) which principal components include cellulose, hemicellulose and lignin. The production of liquid cyclic oxygenates from such heavy molecules is straightforward therefore, the design of a commercially viable production process of these species is a current subject of investigation [102].

1.3 Investment and research in the field of the internal combustion engines.

This paragraph would collocate and explain why, in the period in which it is advertises a lot the electrification of the propulsion system, have sense to invest to further extent in the field of the internal combustion engine.

Cheah *et al.* [3] affirmed that - the internal combustion engine will continue to improve and remain the dominant technology for the next two or so decades, although we are likely to see an increase in powertrain electrification and the use of nonpetroleum fuels within this period.

An answer was also given, at the Emission Research Conference (DEER), by Byron Bunker, Director of Heavy Duty Engine Center, US Environmental Protection Agency during his remarks in a panel discussion on the role for internal combustion engines in the energy future [16]:

"The future of the IC engine is bright and clear; I don't think that could be any more obvious to all of us". Even while projecting to the future and talking about batteries and electric vehicles, he said, *"When you look at our actual analysis and you look to our projections for the future, 95% or more of the vehicles, all of the heavy-duty vehicles in our analysis are relying on IC engines"*.
By the other way, Hugh Blaxill, Managing Director of Mahle Powertrain, said that the current surge in volume of 4-cylinder engines along with the rapid ramp in direct injection and variable valvetrain technologies across all manufacturers marks the start of a sharp increase in downsized applications and hybrid powertrains.
In the longer term (out toward 2030), Mahle sees increasing downsizing, with a surge in 3-cylinder applications, increasing electrification, and increased use of bio- and gaseous fuels.
David Greene of Oak Ridge National Laboratory put the importance of improving efficiency in the transportation sector in the broader context of an ultimate transition to a different form of energy, i.e., non-petroleum-based for transportation. He said: *"the number one priority, I think, is and should be improving the energy efficiency of the global transportation system."* [16].
If we are going to get to a sustainable transportation system, for 2050 and beyond, probably we should introduce different forms of energy to run the transportation system. However, it is obvious that, the transition process would be a lot easier with a higher energy efficient transportation system.
However, to improve the fuel economy of the propulsion systems, and moreover to meet the targets in terms of both GHG emissions and other pollutants (see 1.1.4), engine should become more robust to fuel variation with new sensor technologies and new/alternatives combustion methodologies. These objectives require, however, a strong research in the field of internal combustion engines.
In this context, I am going to place the research done and described in this manuscript

1.4 **Structure and objectives of this research**

A great deal of research is currently devoted to the development of innovative combustions such as PCCI/HCCI in order to improve efficiency and reduce emissions relative to typical diesel

engines. The aim is to reduce the in-cylinder emissions in order to reduce the load devolved to the aftertreatment devices bringing to higher fuel efficiency and lower costs.

It is logical to think that these changes necessarily bring to specifically "designed fuels" and to new or modified engine hardware in order to make them suitable for the new combustion concepts. However, at this stage of development, it is not possible to define with any certainty the fuel requirements of these engines but it has been suggested that the best fuel will be a minimally refined product that has properties midway between gasoline and diesel [5].

The purpose of this research is to bring a scientific contribute understanding of what approaches are successful in adapting a modern LD DI diesel engine to operate a PCCI with the aim to reduce simultaneously soot and NOx emissions without excessive penalties in terms of HC and CO. The not less important, fuel consumption and combustion noise level, that could be potentially limiting factors, are considered. The approach of this research was essentially experimental combining different type of fuels, injection systems and strategies.

The first part of this work is dedicated to assess the impact of alternatives/renewable low cetane "oxy-fuels" on a modern automotive LD DI diesel engine. The aim is to acquire insight into the influence of cetane number (CN) and fuel oxygen on overall engine performance in a premixed combustion mode (PCCI: Premixed charge compression ignition). Further, more conventional engine control strategies (pilot + main, EGR, etc.) were used. The project was carried out in cooperation with the Technical University of Eindhoven.

The aim of the second part of this work is to study the combustion mechanism improving the mixing process using a port fuel injection (PFI) system. This part, conducted in cooperation with the Politecnico di Torino and Centro Ricerche Fiat (CRF) was founded partially by the Italian University and Research Ministry for through the FIRB Project DM24153.

This research will continue in the future in order to contribute further, to some extent, in the promising field of the low emission high efficient combustion. Finally, I believe that as occurred more times in the past, there will be new breakthroughs that will make the ICE competitive in the coming decades with respect to the alternatives propulsion systems.

2 BACKROUND: ADVANCED DIESEL COMBUSTION METHODOLOGIES AND TECHNOLOGIES

2.1 The advanced diesel combustion concepts: HCCI, PCCI, LTC

In conventional diesel combustion, the typical high compression ratio of the CI engines (14-20), permit the air-fuel mixture to auto-ignite as consequence of piston compression. The processes, which occur between the two moments when the liquid fuel leaves the injector nozzles and when the fuel starts to burn, are complex and include droplet formation, collisions, breakup, evaporation and vapour diffusion. These processes effectively limit the rate of combustion. A part of the air and fuel will be premixed and burn fast, but for the larger fraction of the fuel, the time scale of evaporation, diffusion, etc. is larger than the chemical time scale. Therefore, the mixture can be divided into high fuel concentration regions and high temperature flame regions. In the high fuel concentration regions, a large amount of soot is formed because of the absence of O_2. Some soot can be oxidized with the increase of in-cylinder temperature. In the high temperature flame region, the temperature can reach about 2200 K, which leads to a great deal of NOx emissions. Thus, for diesel engines, a trade-off between these two emissions is observed, and their problem is how to break through the compromise between NOx and PM emissions. Moreover, as discussed in the previous chapter, since the aftertreatment systems to reduce NOx and particulates are expensive, instead to delegate the emission reduction almost completely to the aftertreatment systems, the ambition is to have both low in-cylinder emissions and high efficient combustions.

This is because of increasing attention has been devoted to the study of the homogeneous charge compression ignition (HCCI) engine. The HCCI concept seems to be the most promising new combustion strategy because it can reduce NOx and soot emissions simultaneously while maintaining high fuel efficiency [36][37][38].

The HCCI combustion process is closest to the Otto cycle and incorporates the advantages of both spark ignition (SI) engines and compression ignition direct injection (CIDI) engines. The ideal HCCI process is characterized by a lean, premixed and homogeneous charge that reacts

and burns volumetrically and slowly throughout the cylinder by piston compression. In particular, the auto-ignition occurs through the cylinder without flame propagation at multiple sites simultaneously. These features lead to very low NOx and particulate matter emissions while maintaining high thermal efficiency. In particular, this avoids the well-known drawbacks of mixing - controlled combustion that cause soot formation in DI Diesel engines. Moreover, it leads to lower gas temperatures, thus reducing NOx emissions [39].

HCCI is the basic idea of advanced diesel combustion. The diesel HCCI combustion strategy is often referred to as *"PCCI concept"* [40], which is based on non-uniform or partially premixed mixtures achieved during a shorter period of crank angle between injection and combustion event than in port injection HCCI strategy. The stratified fuel mixtures present in the cylinder include fuel rich mixture elements, which are effectively utilized to expand load range by preventing instantaneous combustion specific to HCCI combustion. There are various types (and relative acronyms) of advanced diesel combustion strategies such as Uniform Buckly Combustion System (UNIBUS) [41], Premixed Lean Diesel Combustion (PREDIC) [42][43], low temperature rich combustion (LTC) [44] and premixed charge ignition (PCI) [45] that are categorized in the PCCI combustion regime. They are described more in detail in the paragraph 2.3 where are also reported the possible pathways to realize such advanced diesel combustions.
Figure 2.1 illustrates a comparison between diesel HCCI (or PCCI) and conventional diesel combustion, showing typical features of PCCI combustion achieved by early injection timing [12]. HCCI combustion exhibits a two-stage combustion process instead of the conventional premixed-diffusive combustion. Moreover, the HCCI in-cylinder combustion temperature is much lower compared to the conventional one. These aspects are discussed in detail in the next paragraphs.

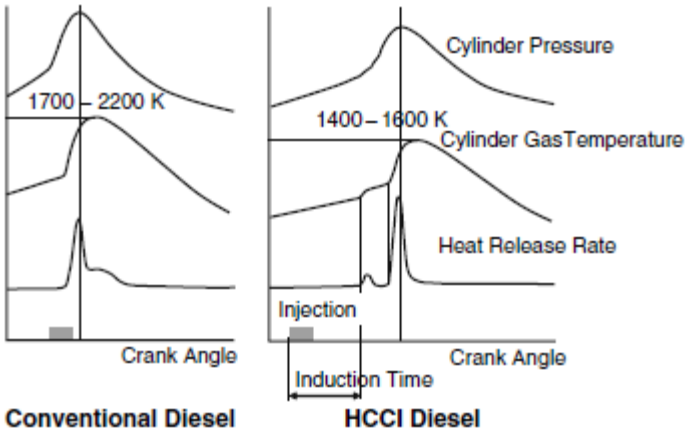


Figure 2.1: Comparison between conventional and HCCI (or PCCI) combustion showing a longer induction time

2.2 Aspects and challenges of PCCI/HCCI combustion

The most typical features, advantages and drawbacks, of HCCI/PCCI combustion are itemized and discussed in the next subsections [12]. In particular, they are characterized by:

- Homogeneous mixture preparation
- Two-Stage Heat Release
- Low NOx and Soot Emissions
- High levels of Noise, UHC and CO emissions
- Combustion control
- Operation range

2.2.1 Homogeneous mixture preparation

Mixture homogeneity, is one of the challenges of the HCCI combustion mode because, it has an effect on auto-ignition reactions that control the HCCI combustion phasing [46] and there is significant evidence that low NOx emissions can be produced even with some degree of mixture inhomogeneity within the combustion chamber.

Therefore, an early injection phasing and a long induction time are fundamental to have a sufficient mixing time before auto-ignition occurs. These characteristics play a fundamental rule in the PCCI combustion to premix fuel, air and EGR gases. A longer induction time between the start of injection and the start of heat release (HR) features diesel HCCI combustion.

The mixture can be prepared either internally (HCCI) [47][48], than externally the cylinder, e.g. with port fuel injection (HCCI-PFI)[54][55][56]. The problem observed when in-cylinder mixture formation occurs is the integration with the conventional DI operations at medium and high loads where HCCI operations are inapplicable (see paragraph 2.2.6). The external mixture formation approach, instead, allows for a better mixing of air and fuel without modifications to the DI system [55][57][58] even if fuel deposit or condensation may occur in the intake manifold.

Homogeneous mixture preparation is most difficult for fuels with reduced volatility such as diesel, which requires very early direct injection or elevated intake air temperatures for low-smoke operation when port-injected. The integration of the external mixture formation with a conventional in-cylinder fuel injection has been also analysed in this work and explained in the Chapter 5.

2.2.2 Two-Stage Heat Release

HCCI combustion mode, as shown in Figure 2.2, features a *Two-Stage Heat Release* combustion one for the low temperature oxidation reactions and the other for the high temperature oxidation reactions. In fact, as the in-cylinder mixture temperature rises during the compression stroke, weak heat release due to the low temperature reactions occurs first, resulting in slight increases in both in-cylinder pressure and gas temperature.

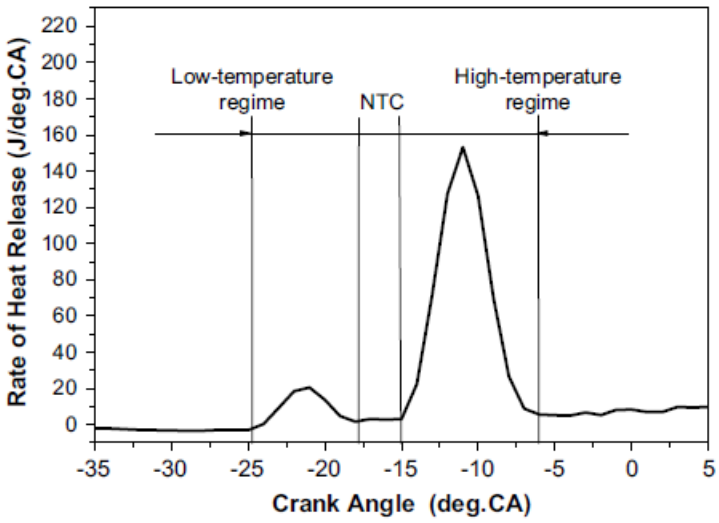


Figure 2.2: Typical heat release curve from HCCI combustion of n-heptane fuel.

The *low heat release (LHT)* is associated with low temperature kinetic reactions. After, the LHT the *high heat releases (HHR)* occurs which is attributed to the negative temperature coefficient (NTC) regime [27]. The NTC, as the intermediate temperature regions between the LHT and HHR, is regarded as being the general characteristic in fully or partially premixed mixture. In this region, though reactions among in-cylinder species are still going on, the heat release is near zero. The duration of NTC decreases greatly with increasing pressure and cool flame temperature because these accelerate the activation of the hot flame region [75]. The temperature range of the NTC area is between 700 -950K [72][73]. In this NTC regime, the overall reaction rate decreases though the in-cylinder temperature increases, which leads to a lower reactivity of the system[10].

Heat release from low temperature reaction is mainly related to the fuel and the engine operating conditions. In particular, in the case of diesel fuels with a relatively high[11]auto ignition tendency or cetane number [76], the LHT curve was observed. In the case, instead, of gasoline-like fuels with a low cetane number (high octane number), LHT is less compared with diesel-like fuels at the same condition. Consequently, heat release from low temperature reaction is too little to observe expectedly from the heat release profiles at most conditions for gasoline-like fuels [28].

[10] Generally, in the literature, NTC region refers to a range of temperature where ignition delay time (ID) increase with temperature, i.e. the slope of ID as a function of $1000/T_{in}$ in an Arrhenius plot from positive becomes negative.
[11] In general, the higher the longer the carbon chain the higher the auto-ignition tendency.

In case of HCCI-DI can be noted also a diffusive combustion due to the directly injected diesel fuel [75]. Oxidation of hydrocarbon fuels mainly takes place via two representing routes shown in Figure 2.3.

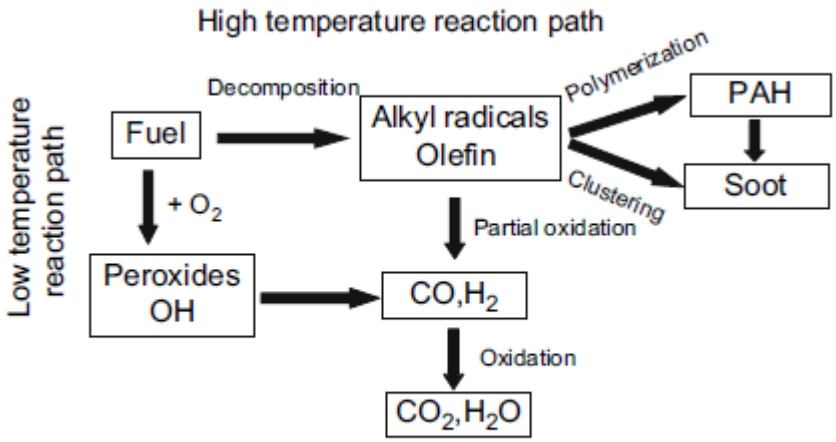


Figure 2.3: Reaction paths of hydrocarbon fuels in low and high temperature reactions [28].

In the *low temperature oxidation (LTO)* reactions are produced intermediate species (CH_2O, HO_2, and O radicals) within the cylinder through abstraction reactions of hydrogen, and auto-ignition, i.e., cool flame reaction, starts by the reaction of OH with RH produced from peroxides such as aldehydes[27]. After a short period, the thermal flame reaction starts, accompanied by the main heat release.

The high heat release rate (RoHR) of main combustion (Figure 2.2) is dominated by the *high temperature oxidation (HTO)* reactions of hydrocarbon fuel through which intermediates such as olefins and alkyl radicals are rapidly consumed. The presence of high concentrations of CH, H, and OH radicals are indicative of high temperature chemistry during the bulk burn [78]. These intermediate species are produced by thermal decomposition reactions including the chain breaking of C–C bonds in the fuel. The in-cylinder mixture is partially or nearly homogeneous when ignition starts, and once high temperature oxidation occurs locally, it triggers auto-ignition instantly throughout the combustion chamber except in the quench layers. The steep pressure

rise produced by the auto-ignition generates intense combustion noise, one of the other concerns of HCCI combustion.

The in-cylinder gas temperatures, which the low and high temperature oxidation reactions start respectively, was investigated [29]. It was observed that for n-pentane the low temperature oxidation (LTO) and the high temperature oxidation (HTO) start at around 790 and 970 K, respectively, independently of equivalence ratio, EGR rate and intake air temperature.

Thus, the in-cylinder gas temperature governs dominantly the ignition process in HCCI combustion. In accordance with Najt and Foster [77], who concluded that HCCI auto-ignition is controlled by low temperature (below 1000 K) chemistry and the bulk energy release is controlled by the high temperature (above 1000 K) chemistry dominated by CO oxidation.

2.2.3 Low NOx and Soot Emissions - Non-Luminous Flame

When EGR is not employed, HCCI combustion is possible only for *Fuel Lean and Low Temperature Combustion*, i.e. in a limited range of air fuel ratio (see Figure 2.6). As shown in Figure 2.1, the peak cylinder gas temperature in HCCI combustion ranges from 1400 to 1600K and is significantly lower than 1700–2200K in conventional diesel combustion. The low cylinder gas temperature suppresses both NOx and soot production, but, on the other hand, involves the slow oxidation reactions that cause misfiring and quenching, resulting in the higher HC and CO emissions as compared with those in conventional diesel combustion. In Figure 2.4 [12] is reported a φ-T map, showing the operating regions of the advanced combustion regimes and a belt-like region for conventional diesel combustion representing the temporal changes of equivalence ratio, φ, and temperature, T, in the flame [79][80]. The advanced combustion regions are located in the left bottom corner away from NO and soot formation areas.

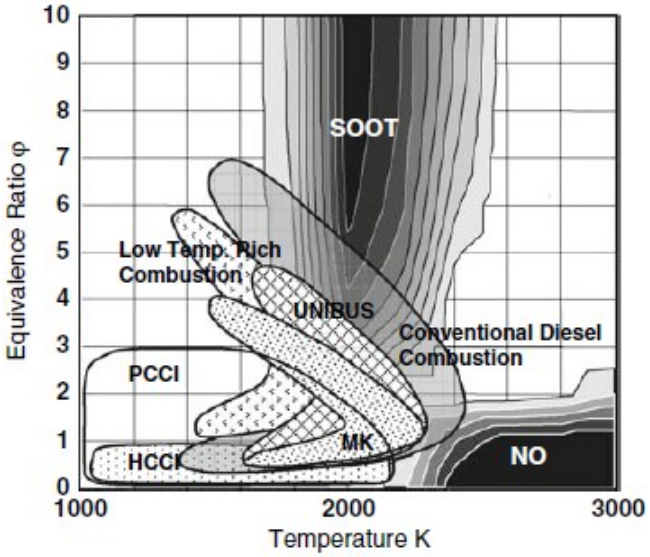


Figure 2.4: Operating regions for conventional and advanced diesel combustion regimes in relation to NO and soot regions [12].

In HCCI combustion, the fuel air mixtures are nearly premixed within the longer induction duration, and as a result optical diagnostics (see Figure 2.5) has shown that advanced low temperature combustion (LTC) initiates simultaneously at multiple sites within the combustion chamber and that there is no discernible flame propagation - *Non-Luminous Flame* [27]

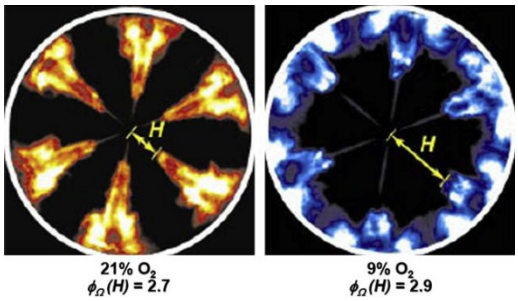


Figure 2.5: Conventional diesel and LTC (engine speed 1200rpm, nitrogen dilution to simulate EGR) [81].

Figure 2.6 [82] illustrates a comparison of NOx emission characteristics between three combustion modes; compressed natural gas (CNG) homogeneous mixture spark ignition combustion, glow plug assisted CNG direct injection combustion, and the premixed diesel combustion, including PREDIC, UNIBUS and PCCI combustion[30]. NOx emissions of spark ignited homogeneous mixture combustion depend on the equivalence ratio as the NO chemistry

suggests. NOx emissions for direct injection combustion remain at high levels from 102 to 103 ppm over a wide range of equivalence ratio, which is common in turbulent diffusion combustion. All the data for NOx emissions of the advanced diesel combustion regimes stay in a domain bounded by two extrapolated lines, for CNG direct injection(not homogeneous) and CNG homogeneous combustion. This means that the advanced diesel combustion regimes are of partially homogeneous combustion. This is the reason why the HCCI in diesel engines are defined PCCI. NOx emissions in PCCI combustion regimes are lower than 100 ppm although the operation is possible only in a narrow range of equivalence ratio (between 0.2 and 0.4).

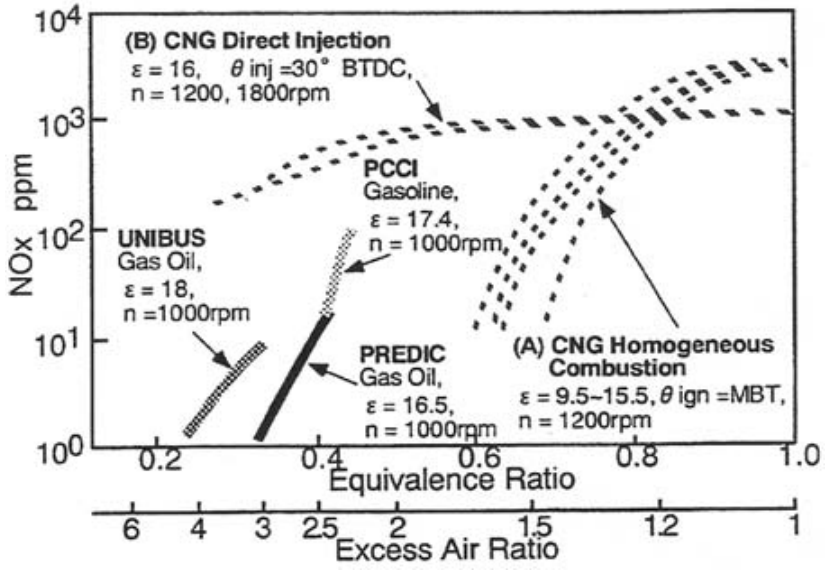


Figure 2.6: Relationships between NOx emissions and mean equivalence ratio for various combustion strategies without EGR [82].

This is why, further researches are needed, in the field of HCCI combustion, to overcome the obstacles that limit its use in the whole operating range of the ICE.

2.2.4 High levels of Noise, UHC and CO emissions

Challenges for HCCI operation are the potential increase in noise, UHC (unburned hydrocarbon) and CO emissions. As with all homogeneous combustion systems and with the early direct injection strategies, the spray wall impingement as well as the low temperature combustion are the major causes for the high HC and CO emissions and high indicated specific fuel

consumption (ISFC). This is why, significant portion of the in-cylinder fuel is stored in crevices during the compression stroke and escapes combustion. Moreover, the burned gas temperature is too low to consume much of this unburned fuel when it re-enters the cylinder during the expansion stroke. This results in significant increase in both HC and CO emissions relative to conventional combustion. In addition, the peak burned gas temperatures are too low (lower than 1400 K or 1600 K) to complete the CO to CO_2 oxidation at low loads, and the combustion efficiency deteriorates precipitously.

This loss of combustion efficiency combined with ignition difficulties limits the effectiveness of HCCI combustion at the lightest loads (see Figure 2.6). At higher loads, the rate of pressure rise can become so large that engine noise increases significantly, and if left unchecked, engine damage may occur [31].

The use of high volatile fuels could be beneficial to reduce HC and CO emissions for medium loads but for very low loads, it could be lead to over-mixed charge increasing more the HC and CO [18]. Moreover, since the exhaust temperature is lower than in conventional diesel combustion, the advanced diesel combustion systems need special exhaust gas treatment systems that are active at lower temperatures to reduce HC and CO emissions.

2.2.5 Combustion control

One of the principal challenges of HCCI combustion is the control of the combustion phasing. Unlike conventional combustion, a direct method for controlling the start of combustion is not available. Instead, the start of combustion is established by the auto-ignition chemistry of the air-fuel mixture. Hence, combustion phasing of HCCI engines is affected by the following factors: auto-ignition properties of the fuel, fuel concentration, residual rate and reactivity of the residual, mixture homogeneity, compression ratio, intake temperature, latent heat of vaporization of the fuel, engine temperature, heat transfer to the engine and other engine-dependent parameters [33]. In this context, the development of advanced combustion electronic control technology is important (see paragraph 1.1.4) [20]. The state of the art of the new advanced combustion suggests investigating more in such field to make effective the combustion control.

2.2.6 Operation range

In addition to the above problems, another fundamental barrier in HCCI development is extending the operating load range whilst maintaining the full HCCI benefit. Extending the operating range is as important as the auto-ignition process. In addition to expanding the HCCI operation to higher load, very light load operation is also limited, because there is insufficient thermal energy to permit auto-ignition of the mixture late in the compression stroke.

Figure 2.7 gives an example of the narrow *Operating Range* of a diesel HCCI combustion in which equal IMEP lines are included. The data obtained at an engine speed of 1500 rpm using a single cylinder test engine with a compression ratio of 18. In this study, n-heptane (CN 56) was injected into the intake charge to eliminate the difficulty of fuel evaporation [34].

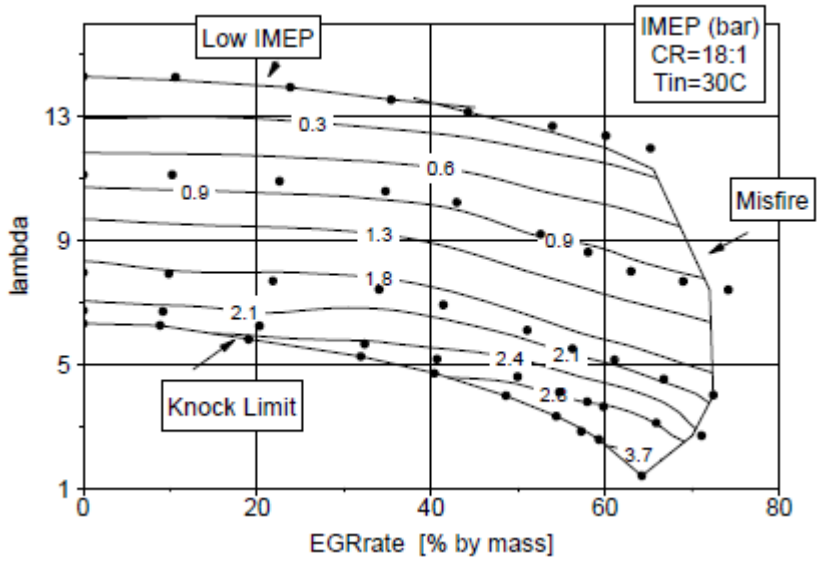


Figure 2.7: Diesel HCCI operating region and IMEP map for a compression ratio of 18 and intake charge temperature of 30°C [34].

The abscissa represents the EGR rate (percentage by mass), while the ordinate gives the overall excess air ratio, lambda, of the cylinder charge. It can be seen, under such operating conditions, diesel HCCI combustion can be achieved over a narrow range of excess air ratios and EGR rates. IMEP is governed mainly by excess air ratio, and 4.0 bar of maximum IMEP is achieved at a lambda of 1.5 and EGR rate of 65%. The upper limit of the HCCI region is bounded by knock,

while misfire occurs at the right and top-right boundary of the region. The richest lambda attainable at zero EGR is approximately 5.0–6.0, significantly high as compared to 3.0 for gasoline HCCI combustion. However, the diesel HCCI combustion can tolerate very high EGR rates, up to 70% by mass.
The operation of diesel HCCI combustion engine depends also on fuel injection timing, which affects the extent of in-homogeneity of mixtures produced during the induction time.

2.3 Strategies to improve the diesel combustion

In the previous paragraph aspects, challenges and the well-known typical features of HCCI/PCCI combustion are explained, whereas in this section, the most known diesel-fuelled HCCI combustion concepts are introduced. Further, there is a classification of what the author thinks about possible strategies to actuate the new combustion concept (fuels, engine architecture, and injection strategies) and finally a hint of the approaches used in this study.
Hereafter are described some of the proposed types of advanced combustion concepts, UNIBUS, PREDIC, LTC, that are actuated in following different methodologies.

Uniform Bulky Combustion System (UNIBUS). Toyota uniform bulky combustion system (UNIBUS) was introduced in 2000 in Japanese Market. The engine is a Toyota 1KD-FTV. It is two-staged injection diesel combustion. The first injection is introduced into cylinder in early compression stroke to form premixed mixture and initiate some low temperature reaction. The second injection is released after TDC to trigger the three combustions. Timing and quantity of the first injection has to be precisely controlled along with boost pressure to avoid premature auto ignition. The main enabling control technologies are common rail injection system and variable nozzle turbo. UNIBUS is only applied under part load and under rpm of 3000. Within UNIBUS operation region, richer mixture is supplied in the first injection under low load condition to ensure there is enough low temperature reaction; while total load is controlled by the second injection
Other UNIBUS studies were done on a 4dm3 four-cylinder diesel engine with a compression ratio of 18 [83] test engine. It employs a centrally mounted pintle-type fuel injector to control

mixture formation and avoid fuel impingement on the cylinder walls. Figure 2.8 [12] shows effects of injection timing on IMEP and emissions under conditions without EGR. High advance in injection timing allows NOx emissions lower than 10 ppm and no soot emissions, but is accompanied by increased HC emissions and lowered IMEP.

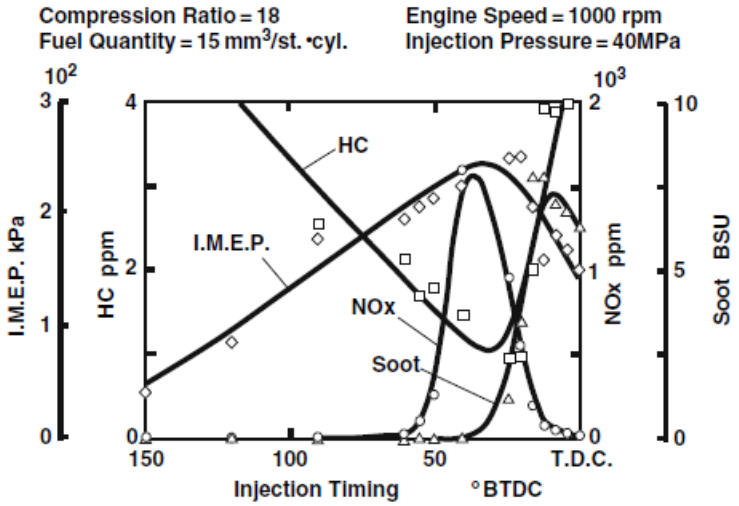


Figure 2.8: Effects of injection timing on emissions and IMEP in UNIBUS combustion [12].

The optimum injection timing of the UNIBUS combustion regime was found to lie between 40 and 60° BTDC. As the figure indicates, the major concerns with UNIBUS are high HC emissions and reduced IMEP. High HC emissions can be attributed to locally distributed mixtures with too lean to burn equivalence ratios and the cylinder wall wetting. Therefore, preventing the injected fuel from impinging on the cylinder walls is an important challenge in UNIBUS combustion regime. The low IMEP, i.e., deteriorated thermal efficiency, is due to premature ignition. The premature ignition phases the combustion in advance respect to the value (6-15°C aTDC) that maximizes the thermodynamic efficiency. Accordingly, the key to improve thermal efficiency is how to postpone the spontaneous ignition timing. Many trials have been made to prolong the ignition delay by focusing on the compression ratio, EGR rate, injection control [48], CO_2 addition, and water injection, all aiming to lower the compressed cylinder gas temperature.

Further studies were carried out looking at the possibility of using a second injection closer to TDC to trigger the combustion, which reduced the NOx benefits but also the fuel consumption.

Low levels of fuelling and low injection pressures were regarded as being most appropriate to limit wall wetting and knocking with this particular injector nozzle.[35]

Premixed Lean Diesel Combustion (PREDIC) is a diesel HCCI combustion concept and employs an early injection strategy [43] [82]. A single cylinder test engine with a displacement of $2dm^3$ and a compression ratio of 16.5 was operated using a fuel with a cetane number of 19 at an engine speed of 1000 rpm. Two injectors were mounted on the sidewalls of the combustion chamber so that the sprays could evolve across the combustion bowl, minimizing the spray impingement on the walls.

Figure 2.9 shows the effect of injection timing on NOx emissions for different excess air ratios. For each excess air ratio, a set of three data plots forms a short curve indicating a range of injection timing in which heat release occurs moderately near TDC with substantially low NOx emissions. The combustion mode observed here was denoted as PREDIC. If the injection timing is retarded beyond the end of the curve, excessive and harsh combustion-knock critical to the operating limit occurs because the shorter induction duration produces much heterogeneous mixture distribution, causing fuel rich mixtures to ignite earlier. Conversely, when the injection timing is advanced earlier beyond the opposite end, the engine suffers the unstable ignition and eventual misfire because the long induction period generates more uniform mixtures that are too lean to burn. This suggests that non-homogeneous mixtures are desirable for PREDIC to assure stable spontaneous ignition. Thus, the extent of the homogeneity of the mixture is an important parameter to determine ignition timing together with the overall equivalence ratio. When the overall excess air ratio is decreased to 2.5, the injection timing has to be advanced to 120° bTDC to achieve PREDIC. The injection timing appropriate for PREDIC is limited in a very narrow crank angle window of less than 10◦CA for each excess air ratio.

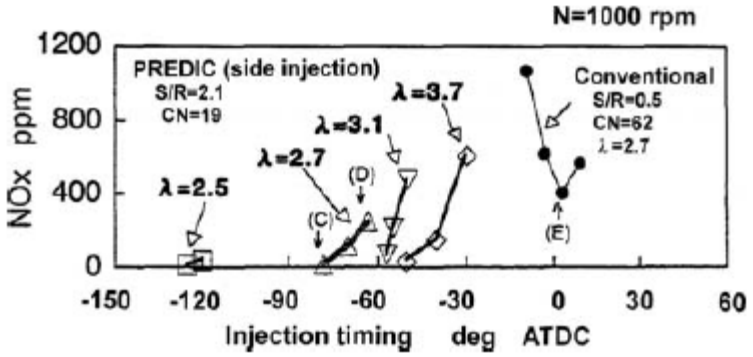


Figure 2.9: NOx emission characteristics of PREDIC (without EGR) [43].

Modulated Kinetics (MK) combustion strategy is based on significantly retarded fuel injection timing and high EGR rate, and requires auto-ignition to occur after the end of fuel injection, allowing lean and partially premixed mixtures to be formed before auto-ignition [85]. Nissan modulated kinetics (MK) combustion mode is introduced to market in 1998 in Nissan engine. In this case, there is a single injection after TDC. The retarded injection along with high EGR ratio prolongs the ignition delay. At the meantime, no re-entrant bowl in combination with high swirl facilitates the dispersion of the injected fuel outside of the piston bowl. Therefore, the mixing time scale is shorter than the auto-ignition time scale, and HCCI combustion occurs. MK mode achieves first success at low load condition, and engine switches to regular diesel operation at high loads. In the effort to expand the MK operating range, one key technical issue is the relationship between injection duration and ignition delay. In order to make the ignition delay longer than the injection duration, high-pressure injection, reduced compression ratio and EGR gas cooling are applied for second generation of MK engine. Normally, retarded ignition and combustion has lower efficiency, but low temperature combustion and low piston head heat transfer mitigates the problem [89].

The characteristics of MK combustion were also investigated using a four-cylinder DI engine [86]. The swirl ratio was set relatively high at four to enhance mixing during the short induction duration. Shown in Figure 2.10 is a comparison between the rates of heat release at three different injection timings and EGR rates. When the fuel is injected at TDC in compressed

charge containing 45% cooled EGR gas, combustion starts after the end of injection, showing a single peak heat release rate in the expansion stroke that is specific to MK combustion.

The authors also show that with cooled EGR and a lambda of about 1.8, the late injection drastically reduces the NOx emissions with the smoke at the same level. Despite the late combustion phasing after TDC, the thermal efficiency penalty is relatively small. Moreover, the authors claim that both the low combustion temperature due to the fuel lean combustion and the reduced flame interaction with the piston surfaces due to high swirl air motion act effectively to reduce heat losses to the combustion chamber walls. HC emissions are lower than in PCCI combustion because of the reduced wall wetting and reduced quench layers near the cylinder walls. The operation of MK combustion is limited to a low-medium engine speed and load range because, at high load conditions, ignition tends to occur before the end of fuel injection due to high cylinder gas temperature

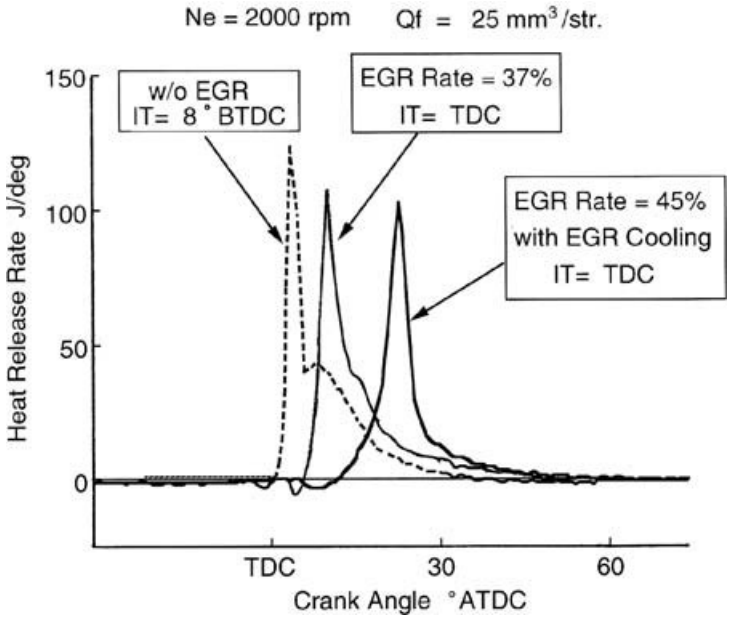


Figure 2.10: Effect of EGR rate and injection timing (IT) on the rate of heat release in MK combustion [86].

Low Temperature Combustion (LTC) in diesel engines consists of fuel injection in which the fuel is allowed to vaporize and mix better with the ambient gas (less rich or even leaner than stoichiometric mixtures) before combustion occurs. A high level of Exhaust Gas Recirculation (EGR) is usually used to reduce the combustion temperature to mitigate the formation of NOx.

Flame temperature under 1800K and equivalence ratios higher than 2 (see Figure 2.4) can lead to soot formation [80]. However, diesel diffusion flames can have complete combustion at temperatures in the range of 1500 - 1600 K, where NOx formation is very low. Therefore, there is a trend towards the development of low-temperature combustion strategies for diesel engines. The initial premixed burn of classical diesel combustion is an example of this type of low-temperature combustion, and if the mixture is lean enough, soot will not form during the low-temperature combustion reaction. The heat release is controlled by the chemical reaction kinetics of the mixture. This introduces new variables due to the factors that are not present in traditional diffusion-burn diesel combustion, where combustion starts in a cetane number-based time delay after the start of the fuel injection [87][88][90][91].

In Figure 2.11 [90] is shown the conceptual mechanism of the LTC. After the fuel injection, fuel evaporation occurs as the hot air has entrained into the fuel jet and mixes. During the fuel evaporation, chemistry becomes active and entrainment continues until ignition occurs. Once ignition occurs, it is assumed that no more air mixes into the core of the fuel jet because the oxygen is consumed in the outer layers of the jet. Consequently, no sooting and low NOx combustion is realized at equivalence ratios below 2 and flame temperatures less than 1800 K. In LTC, with the increase of EGR, the auto-ignition delay period is increased and fuel-air premixing improved. Although liquid fuel penetrates much further into the chamber, the higher energy released from premixed reactions contributes to the intense evaporation of liquid fuel [88]. Since the fuel and air are very well mixed, the amount of oxygen around the fuel molecules is sufficient to prevent pyrolysis and soot formation throughout the jet cross-section.

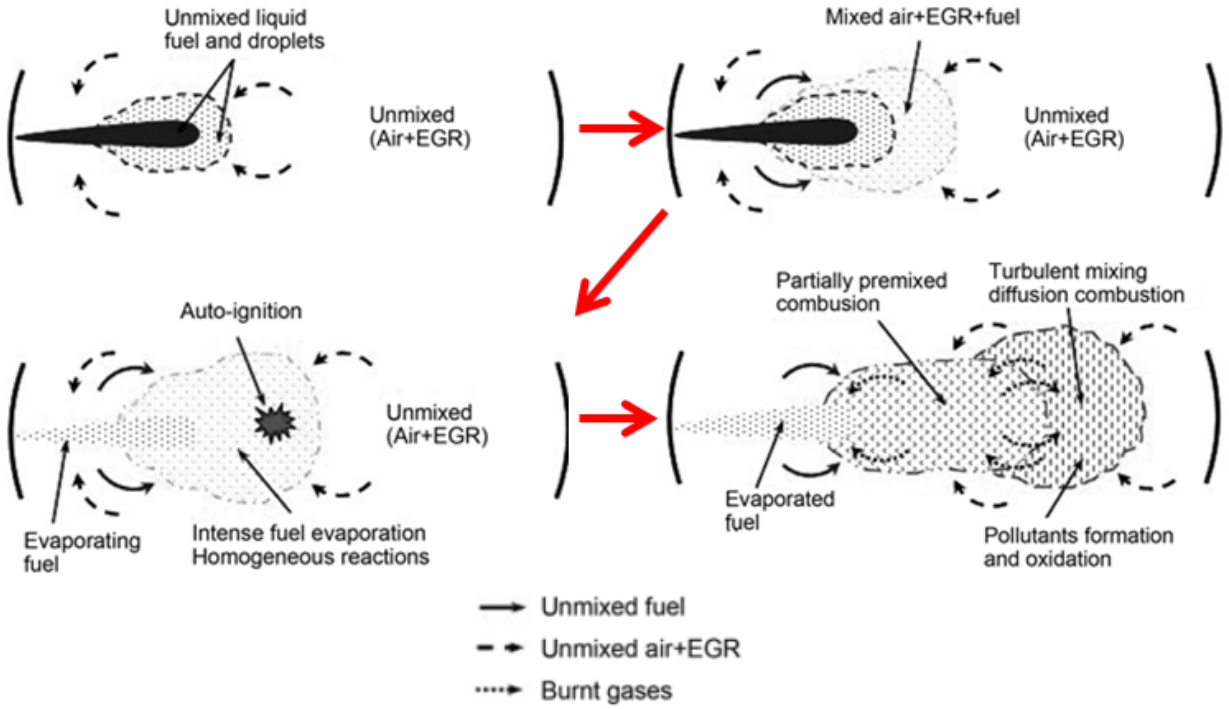
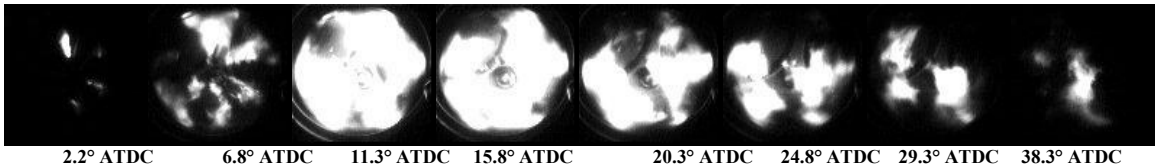


Figure 2.11: Conceptual scheme of low-temperature combustion [90].

Sasaki *et al*. performed experiments on LTC combustion using a 2liter, four-cylinder inter-cooled turbocharged engine with a compression ratio of 18.6. They show the changes in smoke emission and flame images in LTC with the increase in EGR rate, which reduces the air fuel ratio simultaneously [87]. The smoke level increases with the increase in EGR rate, exhibiting luminous colours due to the conventional high combustion temperature. Further increase in EGR rate establishes smoke-less combustion, exhibiting non-luminous flame at air fuel ratios lower than 17.5 realizing a low temperature rich combustion.

Similar experiences were carried out by Bertoli *et al.* [91]. Figure 2.12 shows the flame luminosity evolution carried out with experiments in a single cylinder optical diesel engine operating both under conventional diesel combustion and under low temperature combustion.



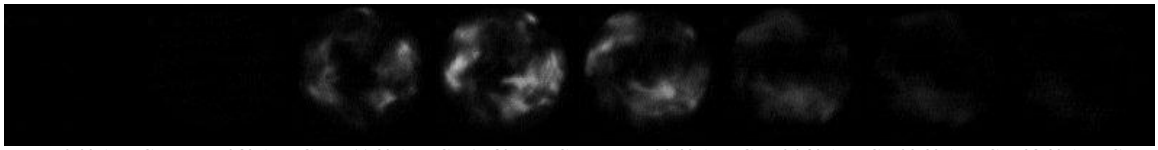


Figure 2.12: Combustion evolution under standard diesel conditions (a); Combustion evolution under LTC conditions (b).

However, albeit a full realization of low-temperature combustion in a practical diesel engine is difficult to realize, with the advanced injection systems (high-pressure multiple injections) and EGR, the standard diesel combustion process is shifting in this direction.

2.3.1 Fuels

In paragraph 2.2.2 is explained why the HCCI combustion, and in particular the low temperature heat release (LTHR) event, is mostly dominated by the chemical kinetics of the fuel/air ratio. Furthermore, researches have shown that the use of conventional fuels (i.e. diesel) is not completely HCCI-like fuels. Thus, to make effective HCCI combustion mode in practical engine operation it could be necessary to reform or design the components, the composition and chemical-physical properties of the fuels. The main parameters that characterize the fuels to HCCI-like fuels are[12]:

- *Cetane number:* high CN fuels feature favourable flame ignitability, and therefore, they extend the lean-burn area for HCCI combustion. Moreover, high CN has a significant potential to promote cold starting, broaden the lean-burn limit, reduces cycle-to-cycle variation and depress HC and CO emissions, but it has a negative effect on the rich-burn limit. *Octane number* has an almost opposite effect to one of the cetane number.
- *Molecular structure:* higher presence of paraffin's enhance the LTHR characteristics, the aromatics inhibit the LTHR effects, olefins and naphthenes have an intermediate behaviour and could both enhance or inhibit the LTHR.
- *Oxygen content:* this factor has a positive effect that broadens the load limit and improves the local combustion efficiency and emissions.

[12] Some of them are described in paragraph 1.2

- *Latent heat of evaporation (LHE):* a large LHE reduce the initial temperature at the beginning of the compression stroke, delay the ignition timing, reduce the maximum combustion temperature and prevent partially knocking combustion.
- *Boiling point and distillation:* a lower boiling point and distillation temperature improves the potential to form homogenous mixtures reducing the local fuel rich zones, then the NOx and PM emissions. On the other hand, at low loads, the lower boiling point promotes misfire or partial burn due to over-mixing increasing the HC and CO emissions.

Considering such characteristics, it is possible to reconfigure the fuel properties and compositions improving the adaptability and compatibility of different fuels for HCCI combustion under a wide operating range [92].
One of the most effective ways to design the fuel characteristics is blend fuels with opposite properties, e.g. adding to the high CN primary reference fuel (PRF) high octane number (ON) fuels. The higher the ratio between ON and CN the higher is the ignition delay [18].
More details, in terms of performance and emissions, of the low CN blends prepared mixing diesel and high octane number fuels are described in detail in Chapter 4

2.3.2 Technologies: injection system, compression ratio, piston bowl.

For high speed LD diesel engines, where high transient conditions occur frequently during vehicle driving operations, to realize a well premixed charge, at least in the low/partial load range, requires a very accurate control of the in-cylinder mixing process and consequently high sophisticated and expensive technologies (like variable compression ratio, variable valve actuation systems, injection rate shaping etc.). Therefore, engine technology improvements represent an important pathway to control HCCI performance, emissions and operating limits. As outlined before, there are several key factors that are fundamental to achieve diesel HCCI combustion and in this section are introduced some technologies able to control them. Anyway, there are reported only some of the technologies and in particular those that are investigated in this work. The effects of the others are widely studied and reported in the literature.

One of the dominant challenges of HCCI is the mixture formation (see paragraph 2.2.1). The mixture can be prepared either internally (HCCI-DI) with an adequate injection phasing and timing [49][50][51][52][53] than externally the cylinder (HCCI-PFI) [54][55][56].

The HCCI - PFI mixture is created in the intake system increasing the available time for premixed fuel evaporation, and then the charge is ignited through piston compression. This allowed to achieving higher engine loads than the in-cylinder mixture formation systems, while preserving part of the HCCI benefits on emissions and without penalizing fuel efficiency.

The integration of the external mixture formation with a conventional in-cylinder fuel injection has been also analysed. The dual combustion system could potentially overcome the limits of low-load operations and allow for a gradual transition between the conventional DI mode at high load and the HCCI external mixture formation at idle and low load [55][57][58][59][60].

Port fuel injection (HCCI - PFI) has been used in early investigations of diesel-fuelled HCCI by Ryan *et al.* and Gray *et al.* [93][94] and Christensen et al. [95]. They investigated diesel-fuelled HCCI - PFI as part of an investigation of variable compression ratios in controlling HCCI with various fuel types. They found that smoke emissions were significant for some conditions, and although NO_x emissions were very low, they were not as low as those with gasoline. These trends were thought to be due because the fuel injected in the intake manifold act as EGR reducing the in-cylinder oxygen content. Moreover, the fuel injected directly inside the chamber is affected by a poorer vaporization due to the higher temperature and pressure inside the cylinder chamber created by the radicalic reaction of the injected PFI fuel. Thus, the oxygen entrainment phenomenon is less effective creating a more inhomogeneous mixture [96] (these aspects are discussed further in the experimental results).

Others found that premixing by port fuel injection has an excellent effect on NOx and soot reduction with premixed gasoline and diesel fuels [61][62][63]. Using Gasoline as PFI fuel, premixing level will drastically increase due to its excellent vaporization and mixing with air [59][60]. On the other hand, diesel premixing showed the limited premixing effects in the emission characteristics and operative range due to the excessively advanced auto-ignition of premixed fuels [61]. In particular, diesel knocking due to uncontrolled self-ignition may occur under high premixed fuel ratio at high loads. Thus the maximum amount of premixed fuel was restricted by these knocking limits [64][65]. Moreover, due to the relatively higher boiling curve

of diesel, problems in terms of intake manifold deposits and wall wetting can cause higher HC emissions and possible dilution of lube oil, respectively.

In order to avoid knock, Ryan and Callahan demonstrated that knock in HCCI diesel combustion can be prevented by reducing the compression ratio. When compression ratio is reduced, the accompanying reduction in temperature rise of the end gas prevents explosive auto ignition from occurring [93]. Peng *et al.* conducted experiments on a four-stroke, single cylinder, variable compression ratio engine using n-heptane, which verified the effects of compression ratio on HCCI combustion. The results showed that the possibility of knocking decreased, with the knock limit pulled to lower air fuel ratio (AFR) region (richer mixture) when compression ratio was reduced from 18:1 to 12:1 [34]. The maximum IMEP attainable on this engine thus increased from 2.7 bar to 3.5 bar. Knock is prevented because, lowering the compression ratio, the in-cylinder gas temperature at TDC is reduced. Moreover, the ignition delay (ID) is prolonged allowing complete injection of all fuel prior to ignition, which is a prerequisite for premixed combustion [97].

Therefore researchers have focused their attentions on potential control methods such as variable compression ratio (VCR) [69][70][71] or variable valve actuation (VVA) to provide the compensation required for changes in speed and load. For example, a variation of the Inlet Valve Closing (IVC) can change the effective compression ratio, which in turn will change the combustion phasing realizing more control in terms of combustion efficiency but also in terms of in-cylinder temperature[66][67][68].

The piston bowl geometry is another parameter that can be adapted to enable the development of HCCI combustion. Researcher demonstrated that in the case of early direct injection, a shallow dish type can reduce the formation of fuel wall-film on the surface of the piston bowl wall leading to lesser soot, HC and CO emissions compared to a standard re-entrant bowl[97]. The BUMP ring combustion bowl combined with multi-pulse fuel injection has been demonstrated to work successfully for HCCI diesel combustion [98].

2.3.3 Strategies: injection timing and phasing, EGR

As mentioned before, diesel HCCI combustion is difficult to prepare because of the lower volatility, higher viscosity and lower resistance to auto-ignition of diesel fuel. Therefore, as mentioned in the previous paragraph, port fuel injection can be used to realize a more premixed charge leading however to more complex design and sometimes to lesser advantages in terms of efficiencies and soot reduction (paragraph 2.3.2).

To overcome the disadvantages of HCCI-PFI, early direct injection (HCCI-DI) strategies can be used. The higher in-cylinder temperatures and densities can help to vaporize the diesel fuel and promote mixing. This allows cooler intake temperatures, reducing the propensity for early ignition. Moreover, only the conventional fuelling system is required for both HCCI and conventional diesel operation. As a drawback, early DI for HCCI produce piston wall and cylinder line wetting due to over-penetration of the fuel. Further, controlling combustion phasing is still a critical issue because injection timing does not provide an effective means of directly controlling combustion phasing as in conventional diesel combustion. Avoid fuel/wall interactions is crucial for achieving high fuel efficiency, reducing HC and PM emissions, and preventing oil dilution. Fuel impinging on the surfaces of the combustion chamber has been proven disadvantageous to HC emissions even for moderately volatile fuels such as gasoline [18].

An interesting diagram relatively to the different injection strategies is reported in Figure 2.13[12]. The diagram illustrates the relationships between injection timing and combustion event for advanced diesel combustion strategies. Different strategies are applied with the objective to reduce the combustion temperature. In particular, HCCI, UNIBUS, and PREDIC are realized by early fuel injection (early HCCI-DI). As a result, the heat release shows two-stage combustion typical of the homogeneous charge.

More retarded injection event are applied in the case of MK, PCCI and LTC. The injection is phased near TDC and in general, high EGR rates are used. In particular, MK combustion involves late fuel injection in high EGR rate environment and the low temperature combustion takes place in the expansion stroke. LTC strategy features intake-air cooling and high EGR rate to prolong the ignition delay time. Consequently, the duration between the end of injection and

the start of combustion is shorter than one in the first group. Generally, they also use high swirl and high injection pressures levels to complete the formation of partially premixed mixtures within this narrow duration. The main differences that characterize the two types of strategies are related to a longer induction period and the two-stage heat release in the case of early HCCI-DI.

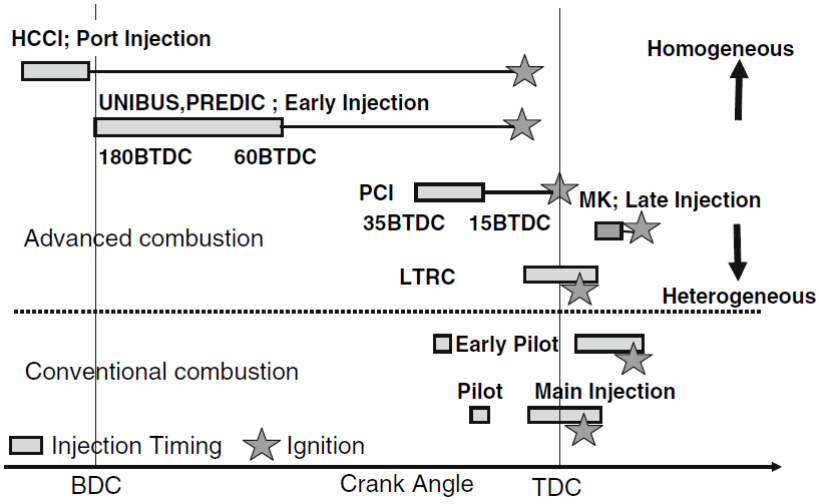


Figure 2.13: Relationship between injection timing and combustion event in advanced and conventional diesel combustion [12].

Concerning the EGR, some effects have been already discussed in paragraph 2.2.4. However, EGR in a compression ignition engine it is generally used to depress the NOx formation whereas in the advanced combustion concepts, EGR could be an alternative method to control the ignition timing and burn rate. EGR has several effects on the combustion. In particular, EGR has: a preheating effect on the inlet charge temperature; a dilution effect with a substantial reduction of the oxygen concentration; a heat capacity effect, increasing the heat capacity of the air, fuel and EGR mixture, leading to a reduction of gas temperature at the end of compression stroke; a chemical effect, inasmuch there persist more radicals that affect the ignition timing, moreover the residual gases (CO, CO_2, NO, H_2O, etc.) take part in the chemical reactions and could lead to some effects on the reaction rates. Results have shown that in the case of HCCI combustion mode, the EGR retard the cool and the high flame heat release. Moreover, with increasing the EGR rate, the combustion duration is prolonged due to the lower combustion temperature; this effect is emphasized for high octane number fuels. Besides, results show that

the EGR tolerability seems to be higher for high cetane number fuel but limited at 45% for CN about 56[100].

In conclusions, in order to give a contribution to reach the HCCI challenges, various strategies that may also move away from truly homogeneous mixtures, including PCCI combustion, where assessed. In particular, in chapter 4 are assessed different kind of fuels, in chapter then a port fuel injection strategy was employed in order to assess their effect of the combustion characteristics.
In chapter 3 is described the experimental setup whereas in chapter and are discussed the experimental

3 EXPERIMENTAL SETUP

This section describes the experimental setup (engine, emission test bench, etc.) used to conduct the research in the field of advanced diesel combustion. In order to acquire insight into the combustion performances, a very useful instrument is a single-cylinder engine characterised by a simple inter-changeability between all components and an independent control of each operating parameter without limiting the others. Vice versa, in the case of multi-cylinder engines, the presence of all auxiliary systems (injection pump, alternator etc.), impose the interdependence among the operating parameters.

Therefore, the experimental activities were conducted on a prototype single cylinder research engine developed at Istituto Motori – CNR. In Figure 3.1 is reported a perspective view of the experimental setup. In the front view shows the single cylinder engine and the auxiliary systems of the engine. Moreover, in the rear view is depicted the panel control of the electronic units.

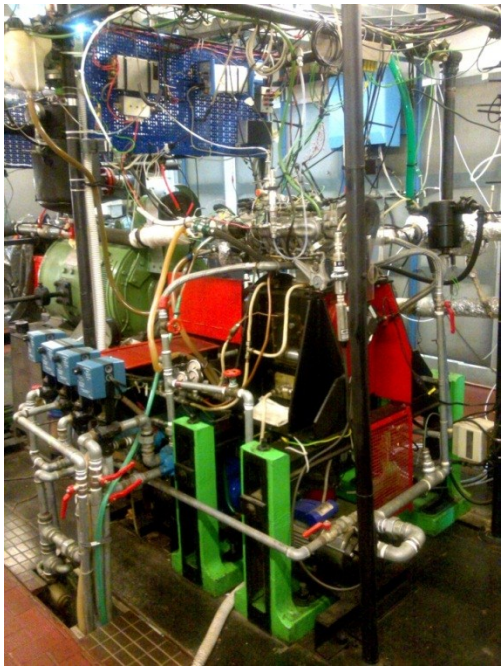


Figure 3.1: Perspective view of the test bench and the single cylinder research engine

3.1 Engine setup

The engine has a modern combustion system design derived from a reference Euro V compliant four cylinders engine. The engine configuration corresponds to the FIAT Multijet 16V architecture, which represents the state of the art of light duty diesel engine technology. In fact, the cylinder head is derived from production series and is a 4-cylinder Fiat JTDM 16V; but it has been modified to work in single-cylinder mode. Connecting rod and piston are derived from production series. The main characteristics are reported in Table 3.1.

Bore [mm]	82,0
Stroke [mm]	90,0
Compression ratio	16,5
Displacement [cm^3]	475
Valve number	4
Injection system	Common rail 3rd generation
Injector	Centered 7 holes microsac

Table 3.1: Main engine geometrical characteristics

The engine is equipped with a fully programmable ECU that permits the operator to modify the fuelling strategy, swirl ratio, backpressure, EGR level, etc. Moreover, the engine was also equipped with a port fuel injector designed and installed specifically to conduct the experiments described in detail in the Chapter 5. The engine system scheme is laid out in Figure 3.2

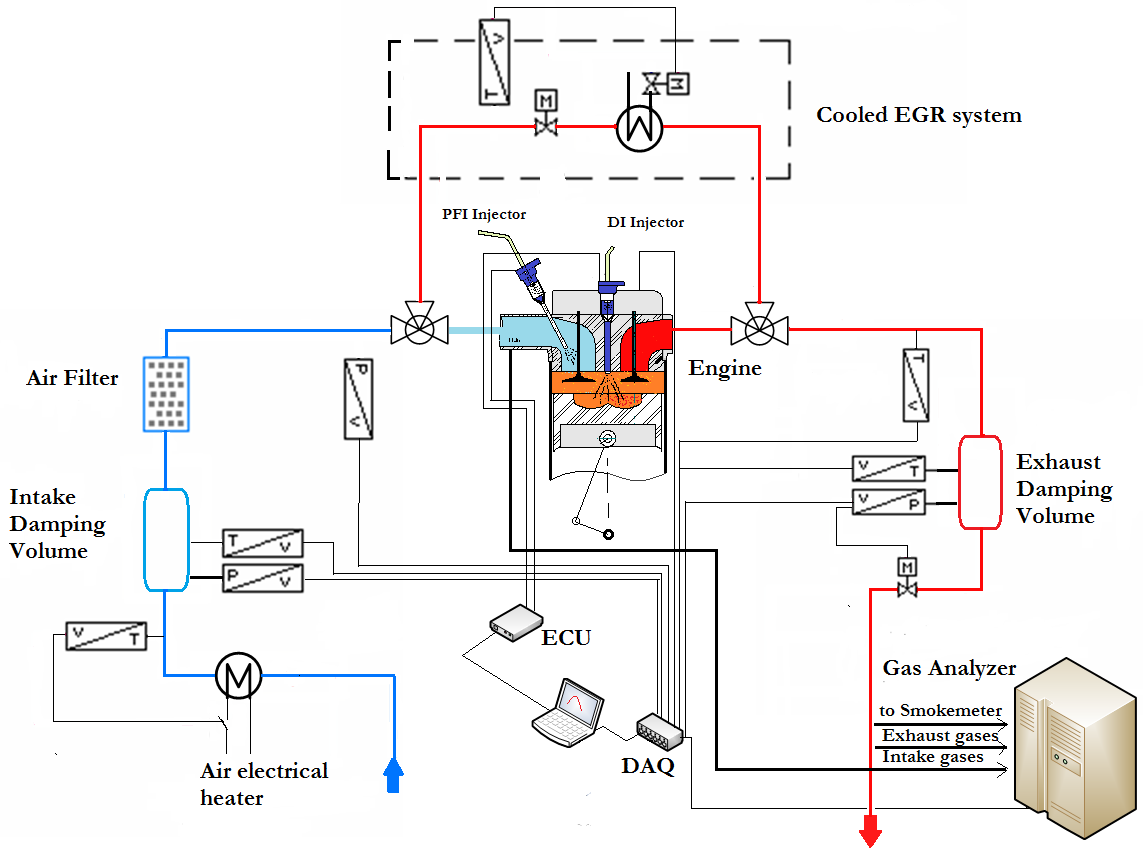


Figure 3.2: Test bench scheme

3.2 Auxiliary systems

The engine is equipped with the following auxiliary systems:

1. Air supply system(Intake, exhaust, EGR)
2. Fuel supply system
3. Cooling system
4. Lubricating system

1. The intake pressure is generated by an external supercharge system connected with the intake line of the engine. Moreover, as depicted in Figure 3.2, an air electrical heater is mounted in the intake line before the manifold. This permits to control the air temperature and pressure in a wide range of temperature values (10÷100°C) and boost pressure values (0÷4.5 bar).

The exhaust line, instead, has been realized in order to simulate the presence of the turbocharger. Therefore a damping volume and, downstream, a throttle valve have been placed. Throttling the valve, by means of the ECU, it is possible to regulate the engine backpressure. The cooled EGR line has been designed to ensure a fine regulation of exhaust gas temperature at the inlet manifold through a small-size EGR cooler. An external water circuit, automatically controlled, in order to regulate EGR temperature independently from the engine water one, feeds the cooler (see Figure 3.2).

2. A low-pressure circuit (tank, balance meter, filter, low-pressure pump, fuel cooler) and a high-pressure 3th generation common rail system (high-pressure injection pump, rail, connection pipe, injector, etc.) constitute the fuel supply system. In order to regulate the rail pressure independently by the engine speed, the injection pump is coupled with an electrical motor. The maximum injection pressure is about 1600 bar and the fuel injector is a “microsac” 7 holes injector. The fuel temperature is automatically controlled by a water-fuel cooler.

3. The cooling system has been realized by an external system including an electrical pump, water cooler, electrical heater and by two, different circuits one for cylinder and the other for the engine head. This approach permits the maximum flexibility in terms of cooling temperature during the engine operations.

4. The lubrication system is ensured by an external circuit including electrical heated tank, pump, filter, oil cooler and by four different circuits to supply cylinder head, crankcase, crankshaft pin, piston and cylinder wall. Therefore, the oil temperature and the pressure can be controlled for each subsystem.

3.3 **Measurement setup**

The instrumentation of the single-cylinder research engine is complicated because the several sub-systems including lubricating, cooling and fuel systems are externally established and controlled (see previous paragraph). Therefore, temperature, pressure sensors and emission

probes have been placed in each critical point of the whole laboratory engine plant in order to measure all the parameters that control the process. In particular, the most important instruments cover the following subheadings:

1. *Cylinder pressure measurement and analysis:* The cylinder pressure is carried out with a piezo-quartz transducer (Kistler 6121 A1) placed in the glow-plug hole. A shaft optical encoder with a maximum angular resolution of 0.1 crank angle degree (AVL 365C) is used for the measurement of the engine speed (rpm) and for the synchronization between crankshaft angle position and the acquired in-cylinder pressure. The signals are amplified acquired and elaborated by a DAQ system (AVL IndiMicro).
2. *Fuel flow and injection pressure measurements:* The fuel consumption is performed by means of a gravimetric balance (AVL 733). A separate fuel supply line has been implemented for the port fuel injection in order to permit the injection of different kind of fuels respect to the direct injection. The measurement of the fuel injection pressure and temperature are obtained by a piezo-resistive transducer (Kistler A4067 A2000) mounted into the connecting pipe between rail and injector, while the energizing current that drives the injector is acquired by a current sensor (MicroSwitch 9617).
3. *Intake, exhaust and EGR systems:* The flows in a single-cylinder configuration (intake, exhaust) are highly pulsating and require special setup and instrumentation considerations to provide reliable and accurate measurements. The intake airflow measurement is performed by a volumetric air flow meter. The characterization of air condition in the intake manifold, in terms of dynamic pressure and temperature values, is performed by a piezo-resistive absolute pressure transducer for instantaneous boost pressure measurement (Kulite ETL193-190M) and by a PT100. A gas-sampling probe has been also installed to measure CO_2 and O_2 inlet concentrations in order to quantify the EGR rate in terms of CO_2 ratio. In the exhaust line, temperature and pressure are measured, immediately downstream the exhaust valves, by a K-type thermocouple and an instantaneous cooled piezo-resistive absolute pressure transducer (Kulite EWCT-250/312M).
4. *Lubricating and cooling system:* The pressures and temperatures of the water cooling system and of the lubricating system are measured in order to control them in real time and control them by means of PID controllers.

5. *Exhaust emission measurement and analysis:* The gas sampling probes have been installed in the intake and in the exhaust lines in order to measure the EGR rate and the engine out emissions respectively. In particular, in the intake manifold are measured the O_2 and CO_2 concentration whereas in the exhaust line are measured the HC, CO, NOx and PM (in some tests are measured also the nanoparticles) concentrations. In Table 3.2 are reported the devices used for the measurements of the intake and the exhaust gases.

Emissions	Working principles	Model
Carbon monoxide (CO)	Non dispersive infrared analyser(NDIR)	Rosemount 880A
Carbon dioxide (CO_2)	Non dispersive infrared analyser(NDIR)	Hartmann Braun URAS10E
Nitrogen oxides (NO, NO_2)	Chemiluminescence detector	Ecophysics CLD700
Unburned hydrocarbons (UHC)	Flame ionization detector(FID)	ABB AO2020
Oxygen (O_2)	Paramagnetic detection analyser	Hartmann Braun MAGNOS 6G
Particulate matter(PM)	Filter paper method	AVL 415S
Nanoparticles(#PM)	Differential Mobility Sizer(DMS)	Cambustion DMS500

Table 3.2: Emission measurement instruments and their working principles.

The gaseous emission measurement set up is equipped with a sample conditioning system. The purpose of the emission conditioning system is to provide a clear and dry exhaust stream to the analysers. The conditioning system removes the particulate matter (PM) and water content from the exhaust stream before it reaches the emission analysers. The raw exhaust gas is transported from the sampling location to the conditioning unit in a heated sampling line in order to prevent any water/UHC condensation in the line. The sample gas are further heated (180 - 200°C) before they reach the UHC, NOx analysers. Besides, the sample passes through the refrigerated unit where any suspended water droplets are removed before they reach the CO, CO_2 and O_2 analysers. For the smoke emissions, no separate conditioning unit is typically used. The smoke meter is normally a self-contained unit and does not require any additional conditioning system.

As explained in Chapter 0, greater attention is focused by the legislation on the emitted nanoparticles (see Figure 1.5). For this reason, it is worth to give some details of the instrument used to measure them. The other devices are well known and more details can be found in the literature.

In this research, some comparisons have been made between different fuels and strategies in order to evaluate their effect on the number and size of the nanoparticles.

The sizing and the counting classification of the particles were performed by a Differential Mobility Sizer (DMS500) which measurement principle is based on the deflection of electrically charged particles combined with electrical counting. Particles enter the DMS500 via a cyclone, which removes particles bigger than the maximum measurable particle size of the instrument (1000nm). Then the sample gas passes through a corona discharge charger then the classifier column (Figure 3.3). Particles are electrically charged by collision with air ions, in a process known as diffusion charging. The charged particles flow within a particle-free sheath flow, which is a uniform, cylindrical laminar column of air, designed to carry the charged particles in a predictable manner. The particles are then deflected towards grounded electrometer rings by their repulsion from a central high voltage rod. In particular, they are subjected to a radial electric field from a central high voltage electrode, which repels the particles towards the electrometer rings. These measure the electrical current from the arrival of charged particles, and thus their mobility.

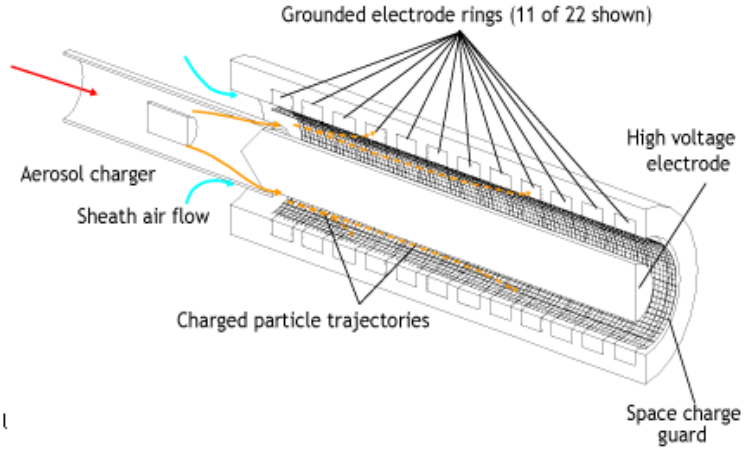


Figure 3.3: Scheme of the DMS500 classifier column and charger

Particles are detected at different points throughout the column, depending upon their aerodynamic drag/charge ratio. Particles which are of low electrical mobility are repelled to the outside slower than highly mobile particles, and hence will travel further down the column before impinging upon one of a 22 electrometer rings along the length of the column. The particles yield their charge to the electrometer amplifiers and the resulting currents are processed

in real time by the instrument's user-interface providing spectral data and other desired parameters. The DMS500 has a fully integrated two-stage dilution and sampling system, this provides primary dilution at the sampling point to avoid condensation and agglomeration issues, and a high ratio in the secondary stage to allow sampling from a very wide range of aerosol concentrations. More details can be found in [101].

4 EXPERIMENTAL CHARACTERIZATION OF LOW CETANE NUMBER OXY-FUELS FOR PCCI COMBUSTION

4.1 Introduction

As outlined in Chapter 2, one of the biggest drawbacks of diesel engines is the so-called diesel dilemma. This refers to the trade-off between NOx and PM, i.e. when attempting to reduce NOx by reducing the combustion temperature, PM emissions increase (e.g. due to poorer oxidation) and vice versa. A lot of research is being conducted into the field of PCCI combustion concepts in order to resolve the diesel dilemma.

In the field of the combustion research applied to the diesel engines, it is known that with conventional diesel fuel, PCCI combustion is difficult to realize due to the relatively high fuel reactivity, which limits the mixing time. Conversely, less reactive, low CN fuels appear to be more tailored to realize PCCI combustion. On the other hand, the main hurdle for PCCI combustion is to extend the operating range to higher loads. In fact, high load PCCI is in general limited by an excessive combustion pressure rise rate. Therefore, more suitable fuels in terms of mixture formation and knock prevention should be explored. In this framework a lot of research and results were carried out in recent past years blending gasoline, and low CN fuels in general, in compression ignition engines ([104]-[107]). As an example, Kalghatgi *et al*. [104], and Han *et al.* [105], have demonstrated the positive effect of high octane number gasoline on soot and NOx reduction in a light duty (LD) compression ignition engine. Among the numerous available papers on the use of low CN fuels in diesel engines for PCCI application, a recent valuable work performed by Kalghatgi *et al*. [120], highlights the influence of the volatile fuel fraction with high resistance to auto-ignition on the unburned emissions in PCCI conditions and due to the over-mixing phenomena, while for fuels with CN<~30 where completely premixed conditions can be reached, volatility and composition become secondary factors on the combustion process.

In this framework, from the fuel side, to limit the over-mixing phenomena for unburned emission control for total premixed air-fuel charges and, simultaneously, to limit smoke emissions when over-rich mixing occurs, low CN oxygenated fuels with less volatility than gasoline could be useful to design tailored blended fuels for PCCI engines. Indeed, it is well known that oxygenated fuels have an intrinsic capability to reduce soot emissions, independently from the engine technology and the combustion mode (e.g. diffusive versus premixed).

Therefore, the adoption of low CN fuels containing intra-molecular oxygen and with boiling temperature range close to the diesel fuel could have potential to improve PCCI performance both at low as at medium/high load conditions [102]. On the other hand, although there are many papers available, which provide valuable information on gasoline/diesel blends ([104]-[109]), there is little information on the use of low CN oxy-fuels in diesel blends [110]. This makes the use of low CN oxygen fuels an interesting route to improve the applicability of PCCI combustion in diesel engines.

The goal is to acquire insight into the influence of cetane number (CN) and fuel oxygen on overall engine performance in PCCI combustion mode. Accordingly, this chapter focuses on providing an overview of the low cetane number oxy-fuels capabilities to improve both diesel and PCCI combustion.

Accordingly, in this study, a commercial, premium quality gasoline and a cyclic oxygenate (e.g. cyclohexanone) were selected as low CN fuels to blend with diesel fuel. The oxygenate in question, cyclohexanone ($C_6H_{10}O$), is a low reactive cyclic oxygenate (cyclohexanone – CYCLOX) that can be produced from lignin (e.g. via depolymerisation) and thus has the potential to be renewable [102].

To assess the impact of cyclohexanone on diesel combustion and pollutant emissions, a parametric test program was carried out in a joint project between Istituto Motori (Naples) and the University of Technology Eindhoven.

The impact of the blends on the engine combustion has been assessed, i.e. in terms of speed and load range and using conventional engine control strategies such as EGR, injection pressures, splitted injection, etc. To highlight the effects of the oxygen content presence in the fuel blends, were prepared and blends with same CNs and different oxygen content (gasoline/diesel and

CYCLOX/diesel). Since gasoline and CYCLOX have different boiling temperature characteristics, the fuel oxygen content effect on combustion cannot be completely isolated from the volatility effect. However, these factors do not affect the investigation mainly aimed to the evaluation of the CYCLOX combustion characteristics. It was assessed that low CN oxy-fuels could act as enablers for PCCI combustion, outlining that the low CN and the oxygen content works together to control the smoke emissions. The research was conducted in a research LD single cylinder diesel engine described in Chapter 3.

4.2 **Fuels**

As stated before, the aim of the study was to characterize the combustion performance of low CN fuels in blend with diesel. Consequently, a commercial, high-quality diesel fuel was chosen as reference fuel, while a premium quality gasoline was chosen as the most common fuel low CN fuel and CYCLOX as low CN oxygenate fuel.

Diesel, gasoline and cyclohexanone were blended into five mixtures, with varying cetane number or oxygen content. The physical and chemical characteristics of the used fuels are reported in Table 6.1. Part of this table is reported in Table 4.1.

Fuel properties	Commercial Diesel	Commercial gasoline	Cyclohexanone
Density @ 15°C [kg/m³]	850	720	950
Viscosity @ 40°C [mm²/s]	3,1	0.5-0.75	4.9
Estimated Cetane Number	~56	~10	~10
Lower Heating Value [MJ/kg]	42,5	43	35
Distillation [°C]			
IBP	-	-	155
10% vol.	222	45	-
50% vol.	276	105	-
90% vol.	329	155	-
95% vol.	345	-	-
FBP	358	190	155
Oxygen [molar%]	0	0	16.3

Table 4.1: Fuel properties

It is worth to note that gasoline and CYCLOX respect to gasoline have a much lower CN (~10). Moreover, the gasoline and diesel are not pure fuels but mixtures of paraffinic and olefinic compounds whereas the CYCLOX is a single component fuel (such as n-heptane and ethanol- see Chapter 5). Accordingly, the distillation curves of the three neat fuels listed in Table 4.1 are plotted Figure 4.1. The single component fuels (CYCLOX) are characterized by a boiling point rather than a boiling trajectory, in fact, one of the advantages to operate with pure fuels is to have well defined fuel characteristics.

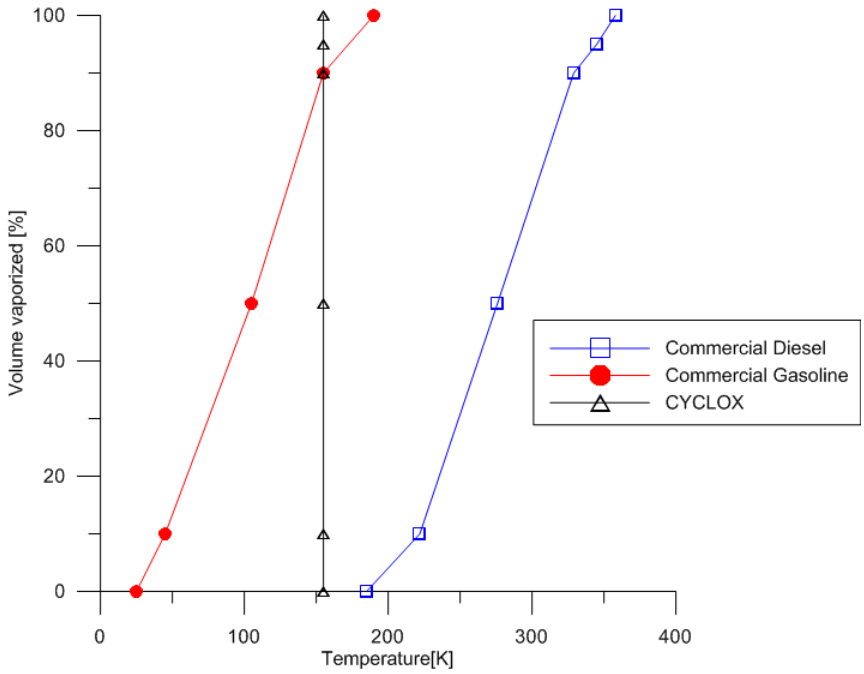


Figure 4.1: Boiling curves of the neat fuels

The estimation of the CN for the blends was computed using Kay's mixing rule [111], which dictates that CN is a molar average of the compounds in the mixture. In particular:

$$CN_{mix} = \sum_{1}^{n} x_i \, CN_i$$

Where, x_i and CN_i represent the molar fraction and the CN of the *i*th-fuel while *n* represent the maximum number of fuels used for the blend preparation.

The blends were formulated such that an equal step size in CN was achieved, namely CN 20, 38 and 56 (see Table 4.2). The CN20 and CN38 blends were prepared for both diesel-gasoline and diesel-CYCLOX, in order to discern the effects between CYCLOX and gasoline.

Blend Properties	**Blend1**	**Blend2**	**Blend3**	**Blend4**	**Blend5**
Fuels	Diesel	Diesel plus Gasoline	Gasoline plus Diesel	Diesel plus CYCLOX	CYCLOX plus Diesel
Blend name	D	DG	GD	DC	CD
Mixing ratio [% vol.]	100	69/31	29/71	77/23	38/62
Estimated CN	56	38	20	38	20
Lower heating value [MJ/kg]	42.5	42.6	42.8	40.7	37.7
Aromatic content [wt.%]	21	24.7	29.5	16.1	8

Table 4.2: Blend properties

Before the presentation of the results, a disclaimer is added pertaining uncertainties regarding the blends. The volatility and the aromatics of the CN20 (Blend 3 and 5) and CN38 (Blend 2 and 4) blends are not equal and could partially have affected the results.

The potential impact of volatility is that higher volatility fuels (e.g. gasoline) can evaporate from hot engines surfaces much better than lower volatility fuels (e.g. CyclOx), which could help prevent UHC emissions.

A second uncertainly is related to CN. It is stressed that for the estimation of CN utilizing a linear Kay's mixing rule, there is an unknown uncertainty, particularly in the low, gasoline-like, CN regime. This is explained by the fact that in the diesel-like CN regime (CN>30) the volatility and the aromatics are less effective on the auto-ignition tendency, thus on the ignition delay, whereas, in the gasoline-like regime (CN<30), the aromatic content and the volatility play an important rule [120]. In particular, the auto-ignition (and therefore the ID) behaviour depends strongly on the chemical structure and behave very differently compared to aromatics as operating pressure and temperatures changes, that explain the possible CN differences.

Therefore, for the gasoline/diesel with CN20, due to its higher aromatics and volatility compared to the diesel/CYCLOX, the estimation of the CN is less accurate.

This suspicion is supported by the difference in ID for the two CN20 blends, e.g. see Figure 4.5.

4.3 Test points and procedures

The tests procedure has been performed in order to characterize and evaluate the fuel effects in terms of performance and emissions either in PCCI combustion mode either in conventional combustion mode.

The chosen reference test points for this campaign are reported in detail in Table 4.3. They were chosen because they are the most representative operating points of the real engine of equal unit displacement during the UDC sub-cycle of the NEDC homologation cycle. To confirm this, Figure 3 shows the position of the selected points in the speed-load plot of a vehicle with 1400 kg of inertial mass, equipped with the corresponding four-cylinder engine over the UDC+EUDC (NEDC) cycle. Moreover, the MBF50% of the reference points is such that the combustion phase maximize the thermodynamic efficiency.

Test point[13]	RPM [1/min]	IMEP [bar]	BMEP [bar]	MBF50% [CA_aTDC]
1500x3(2)	1500	3.2	2	12
1500x7(5)	1500	6.9	5	15
2000x3(2)	2000	3.2	2	12
2000x7(5)	2000	6.9	5	15

Table 4.3: Reference values of the test points; the BMEP value refers to the real four-cylinder engine.

[13] The values inside the parenthesis are referred to the BMEP value. The graphs that follows, sometimes refer to IMEP other times to BMEP (i.e. 1500x2 or 1500x3).

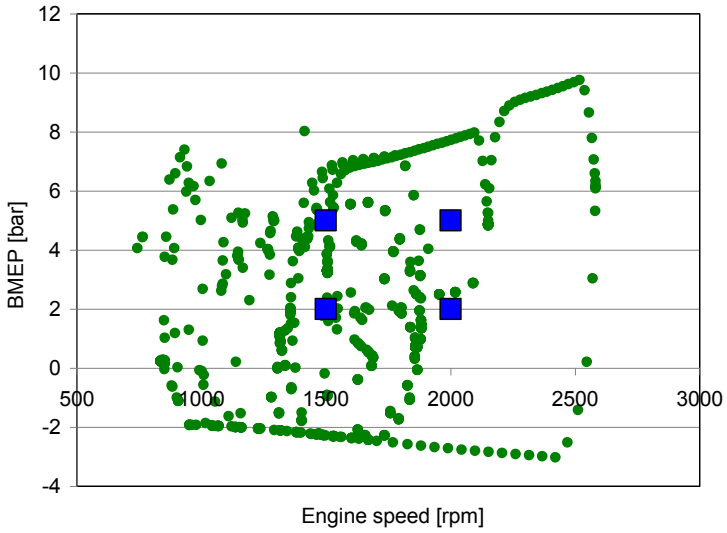


Figure 4.2: Position of the stationary operating points in the speed-load plot of a vehicle with 1400 kg of inertial mass, equipped with the multi-cylinder engine over the UDC+EUDC (NEDC) cycle.

The aim is to acquire insight into the influence of fuel oxygen and CN on the overall performance of a LD DI CI engine in both PCCI and conventional CI mode. The PCCI tests were carried out without the use of a pilot injection or EGR, in order to isolate the influence of the different fuel characteristics.

The five blends were prepared to have different characteristics pertaining to fuel oxygen content and CN. This permit to separate the CN and the oxygen effect on the performance and emissions:

- varying CN at a constant fuel oxygen content
- varying fuel oxygen content at a constant CN

Besides, in order to have a complete screening of the CN and oxygen impact on the combustion characteristics, the different blends has been subjected to an extensive experimental procedure varying the operating conditions:

- ✓ SOI sweep in PCCI combustion mode.
- ✓ EGR sweep with conventional diesel combustion
- ✓ PCCI application with low CN

The procedures are well explained in the corresponding paragraph where also the results are discussed.

Moreover, in the literature, many times when PCCI combustions are performed, any limits are considered, for example, the fuel consumption increase or the combustion noise level or the COV, etc., that most of times limit the practical application of this combustion mode. Therefore, during the test were also considered and imposed the operative limits reported in Table 4.4.

Parameter	Prefixed limits
ISFC	≤5% of ISFC increase with respect to the EURO 5 standards
Cylinder pressure rise rate	≤80 bar/ms of maximum pressure rise rate for each work point to preserve current comfort standards
Smoke	≤1.5 FSN of exhaust smoke as estimated limit in order to avoid excessive DPF system loading
COV	≤3.5 - 4%

Table 4.4: Prefixed operating limits.

4.4 SOI sweep in PCCI combustion mode

4.4.1 Experimental procedure

In this test campaign, for every blend (see Table 4.2), the tests were executed in two of the four mentioned workpoints, reported in Table 4.3: namely 1500x3.2 and 2000x6.9. 1500 and 2000 are the rotations per minute while 3.2 and 6.9 represent the values for IMEP. The workpoint 1500x3.2 relates to the workpoint 1500x2 for the corresponding four-cylinder engine where 5 indicates the BMEP. The same is for the case 2000x6.9 related to the 2000x5. Furthermore, an injection strategy of one shot per cycle was chosen

Starting from these points, the SOI was varied, while all the other parameters were kept constant. The SOI was delayed until the combustion became unstable and the COV reached its fixed limit (~ 4%). This point was defined as the upper limit. After this, the SOI was advanced

with a step size of 10 °CA until the defined limit (80 bar/ms) for the pressure gradient was reached (see Table 4.4).

4.4.2 Test results and discussions

In this subsection, the following analyses are performed:

- Reference point analysis with fixed IMEP and MBF50%: This analysis is useful to study the effect of fuel chemistry at constant value of thermodynamic efficiency.

- Engine performance trend analysis varying start of injection (SOI) at constant injected energy flow: This analysis is useful to evaluate the operating range of the different blends and to compare the trends.

Reference point analysis with fixed IMEP and MBF50%

1500rpm@IMEP=3.2bar and MBF50%= 12° aTDC

In Figure 4.3, the pressure traces and the rate of heat release (RoHR) are reported for all blends with a fixed MBF50%. For the various blends, differences in SOI are observed, as could be expected for blends with varying CN. The blends with a lower CN require more advanced SOI values to obtain the same MBF50%.
The differences in terms of ignition delay (ID), calculated as the difference between SOI and MBF10%, are reported in Figure 4.5. In this figure, the differences in ID between the blends with the same estimated CN are evident.
As stated before, these can be attributed to uncertainties pertaining the estimation of CN, mainly for the CN20 blends. In fact, CN20 blend lies in the gasoline auto-ignition range (CN<30) where the linear estimation of CN, through the Kay's linear mixing rule, is less accurate. Conversely, for the CN38 blends (diesel auto-ignition range: CN> 30) the CN (i.e. ID) is well predicted (paragraph 4.2) [120].

Therefore, the blends with CN38 show a quite similar pressure traces and SOI values, but with the SOI more advanced compared to the CN56 reference fuel.

For the CN20 blends, the differences become more evident and there are differences between the two CN20 blends. This is due to the high percentage of low CN fuels (gasoline or CyclOx) with diesel, which has a stronger effect on the combustion characteristics. Moreover, the low CN blends are more volatile compared to the reference fuel (Figure 4.1). Nevertheless, in [120], where an extensive study on the volatility effect has been performed, is affirmed that volatility has a lower influence, compared to the auto-ignition quality, on the emission performance.

The compression pressure peaks (Figure 4.3, on the left) are lower and have different shapes, which is due to the differences in terms of heat of evaporation, higher for gasoline and cyclohexanone compared to diesel. In addition, the RoHR (Figure 4.3, on the right) is clearly influenced by the CN and volatility, which lead to better mixing and over-lean areas far away from the injector. This assumption is supported by the emissions reported in Figure 4.4, where higher UHC and CO emissions are shown for blends 3 (GD) and 5 (DG); in particular for the gasoline blend (blend 3; CN20) that support the hypothesis of a certain inaccuracy in the determination of the CN mainly for the blends CN20. Furthermore, also the fuel conversion efficiency appears to be lower for blend 3.

The NOx levels are lower for the low CN fuels (Figure 4.4), which is attributed to the lower temperature reached by leaner conditions in the combustion chamber. This is supported by the RoHR, which shows longer combustion duration and lower pressure rise rates. In fact, the longer ignition delay increases the level of premixing in such a way that the local air/fuel ratio approaches the global lean air/fuel ratio. Under such conditions, the local temperature decreases and therefore NOx too (Kamimoto and Bae, 1988) [80][120][121].

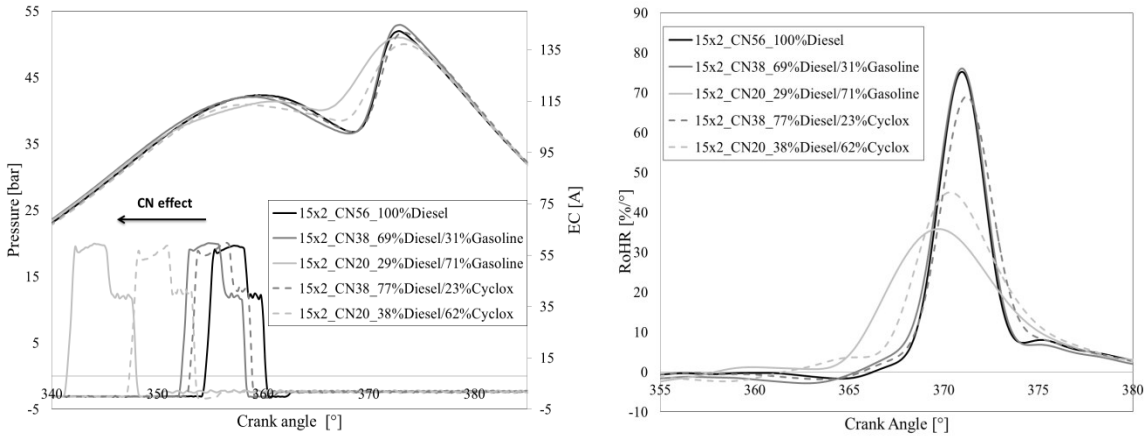


Figure 4.3: Pressure cycle and RoHR comparisons for all blends at 1500 rpm, IMEP= 3.2 bar and MBF50%= 12 °Ca aTDC.

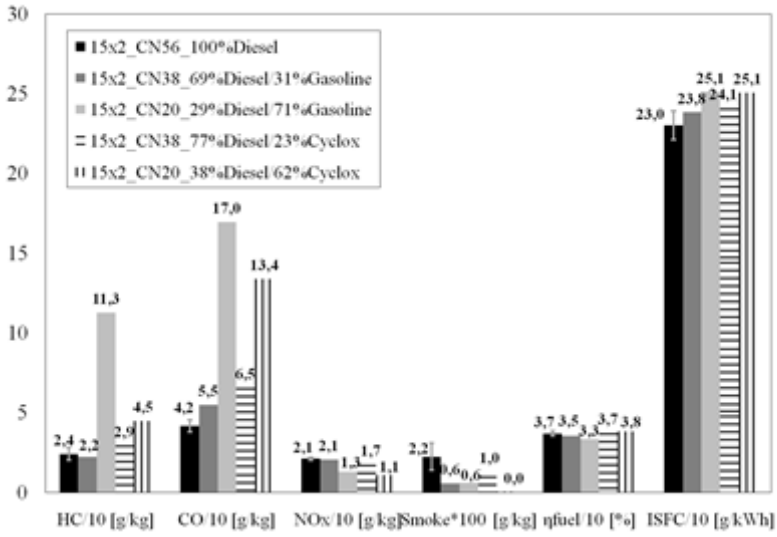


Figure 4.4: Emission Indices comparisons and efficiencies for all blends at 1500 rpm, IMEP=3.2 bar and MBF50%=12 °Ca aTDC.

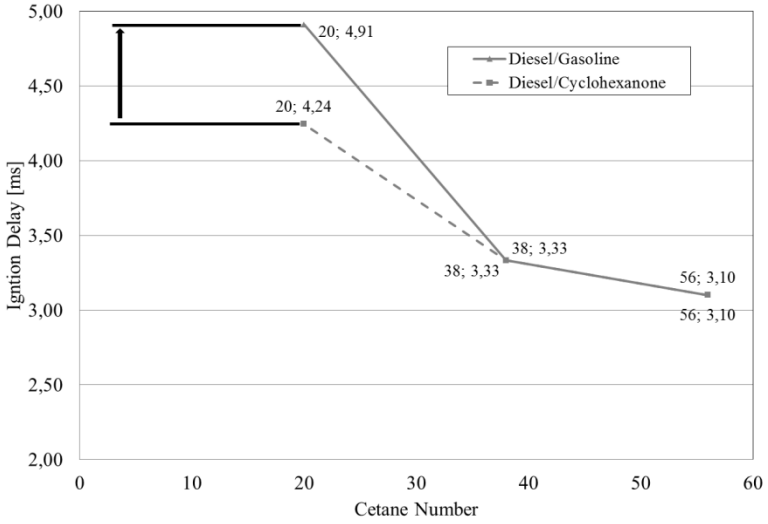


Figure 4.5: Ignition delay versus CN for blends at 1500 rpm, IMEP= 3.2 bar and MBF50%=12 °Ca aTDC.

The effect of the presence of oxygen in the diesel/ CyclOx blends is evaluated comparing oxygenated and non-oxygenated blends with the same CN and benchmarking these fuels to the reference fuel (diesel CN56). In Figure 4.6, the emission indices and efficiencies are plotted for the CN20 and CN38 blends in the reference test point.

For low oxygen contents (Figure 4.6 on the left), e.g. diesel/ CyclOx at CN38, the oxygen effect cannot be discerned from the other effects. For high oxygen contents, i.e. comparing diesel/CyclOx with diesel/gasoline blend at CN20 (Figure 4.6 on the right), the oxygen effect on smoke and UHC emissions becomes more evident.

Instead, the CN effect can be evaluated by comparing the graphs in Figure 4.6, on the left (CN38) and on the right (CN20). The lower CN, which is thought to induce over-lean areas because of ample mixing time (mainly for diesel/gasoline) tend to increase the HC source mechanisms (e.g. fuel outside the piston bowl or in the cylinder crevices, fuel wall wetting). Moreover, the CO formation for CN20 increases much more than for CN38. This is due to the more diluted charge inside the cylinder that lower the temperature then the conversion rate from CO to CO_2. For CN38, the CO emission sources are limited because the main actor is still the diesel fuel (Figure 4.6 on the left: CN38).

The fuel efficiencies for CyclOx blends are inside the test repeatability of the reference fuel, whereas the gasoline blends show a small penalty.

Note that, in the case of CyclOx blends, due to a slightly lower LHV, the fuel efficiency is about the same as the reference fuel but with a higher ISFC.

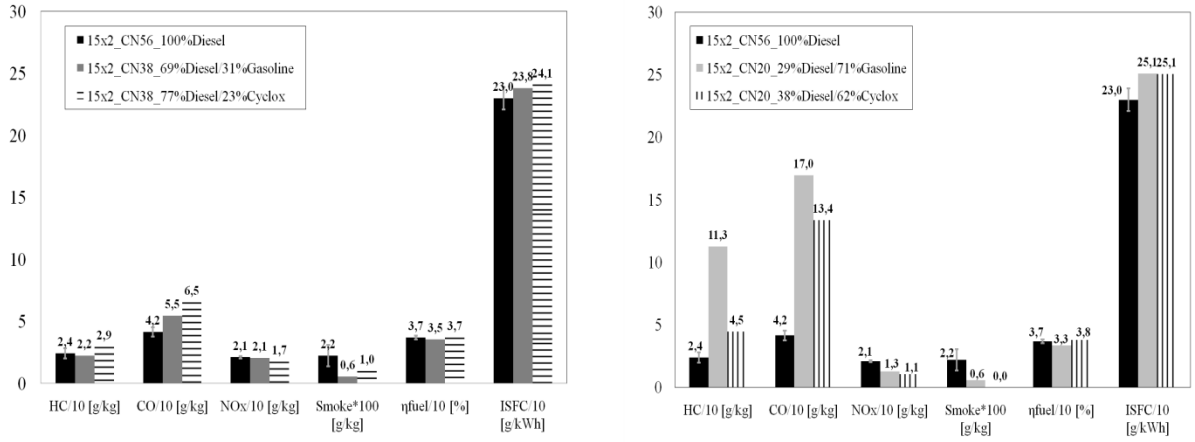


Figure 4.6: Emission Indices and efficiencies comparisons at 1500 rpm, IMEP= 3.2 bar and MBF50%= 12 °Ca aTDC for diesel and CN38 blends (left) and CN20 blends (right).

2000rpm@IMEP=6.9bar and MBF50%= 15° aTDC

Analogous considerations are suitable for higher speeds and loads. In Figure 4.7, the pressure and the RoHR traces are reported for all the blends for fixed MBF50%. The same trends for SOI variation are observed, i.e. blends with lower CN need more advanced SOI at constant MBF50%. The differences in terms of ID are shown in Figure 4.9.

For the pressure and RoHR traces, the CN20 blends, in particular the diesel/gasoline, show a significant difference for the first pressure peak. This is due to the higher heat of vaporization of the blends.

Also for higher loads, although to a lesser extent, it is possible to attribute the over-lean phenomenon thus the higher HC and CO emissions to the increased mixing time and to the higher volatility mainly for decreasing CN.

However, for the diesel/ CyclOx blends, smaller differences in the pressure and RoHR are reflected in the emission indices, which are more or less similar to those from the reference fuel.

The improved characteristics of these blends are attributable to the lower volatility and the reduced mixing time (see SOI) compared to the diesel/gasoline blends. Moreover, also for higher loads, the efficiencies of diesel/CyclOx are comparable to that of the reference fuel (Figure 4.8).

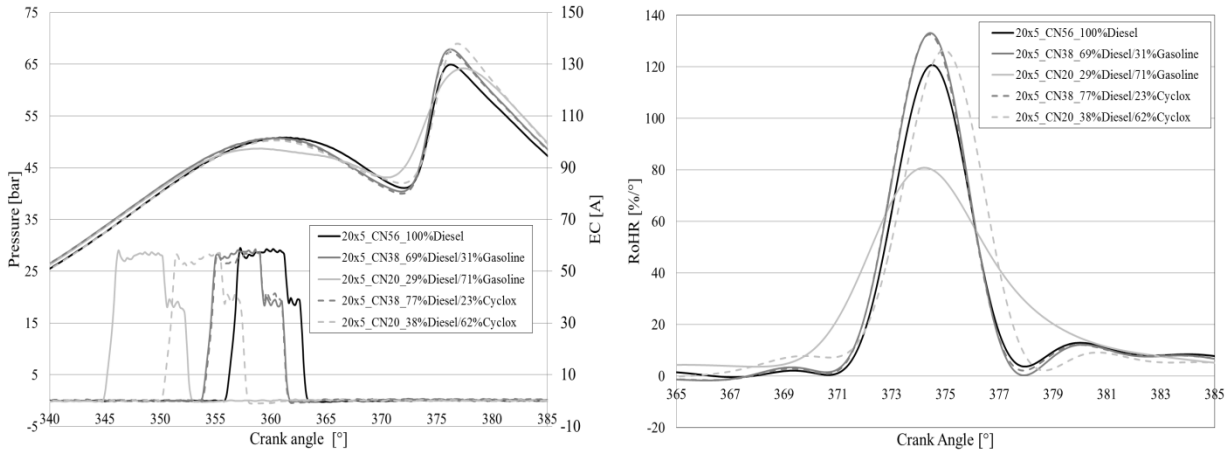


Figure 4.7: Pressure cycle and EC comparison (left) and RoHR (right) comparisons for all blends at 2000rpm, IMEP=6.9bar and MBF50%=15° aTDC.

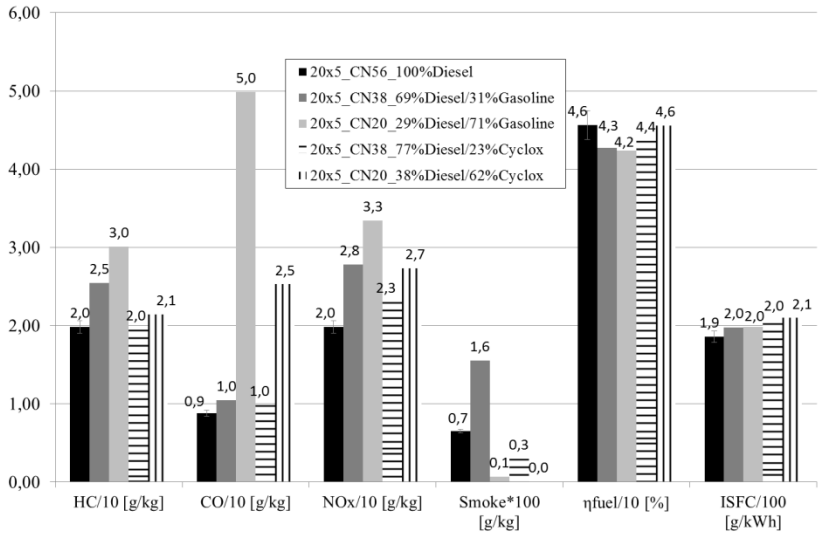


Figure 4.8: Emission Indices and efficiencies comparisons for all blends at 2000rpm, IMEP=6.9bar and MBF50%=15°aTDC.

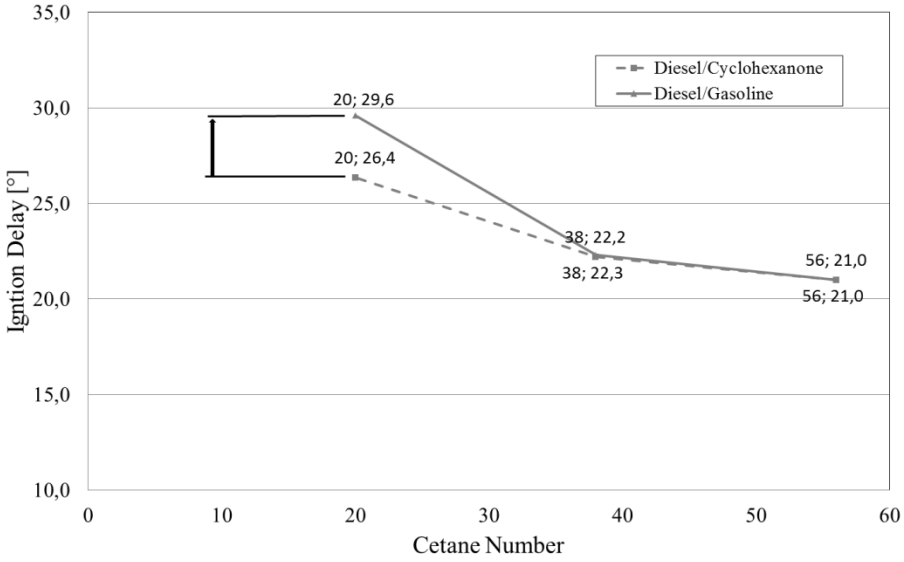


Figure 4.9: Ignition delay versus CN for the blends at 2000rpm, IMEP=6.9 and MBF50%=15°.

Referring to the CN impact, it is possible to state again that also for higher loads there are evidences of both higher volatility and mixing time of the diesel/gasoline blends compared to the others. Therefore, HC emissions increases due to the over-mixing and CO emissions due to the lower combustion flame temperature. The smoke emissions are reduced by the higher level of premixing for all the blends with respect to the reference fuel, but the best results are obtained for the diesel/cyclohexanone blends thanks to the oxygen presence, which enables to reduce the emitted smoke.

Due to the higher premixed conditions for the blends, the higher NOx emissions compared to diesel were not expected. They are due to the higher in-cylinder temperatures for such operating conditions. Further investigations are necessary to have a detail explanation of this trend.

Engine performance trend analysis by varying SOI at constant injected energy flow

1500 rpm; IMEP= 3.2 bar

In Figure 4.10, starting from the reference point (IMEP=3.2bar and MBF50%=12° aTDC) keeping constant the injected energy, IMEP versus SOI variation traces are plotted. The CN38 diesel/CyclOx blend has similar lower and upper limits (i.e. in terms of coefficient of variance (COV) and maximum pressure rise rate) as the diesel fuel, but shows higher values for IMEP at the same SOI values. Moreover, the curve is shifted to more advanced SOI values.

The same effect is noticeable for the diesel/gasoline blend, but in this case, it was not possible to perform the tests in the SOI value range between -40 and -15 °Ca aTDC (note the curve interruption in the Figure) due to excessive pressure rise values (i.e. >>8.9 bar/ °Ca) over the prefixed limit (see Table 4.4) with the risk of engine damage. Similar results have also been observed by other researchers [118]. The operating ranges for the CN20 blends are smaller, as expected, but with the CyclOx/diesel blend appearing slightly more advantageous.

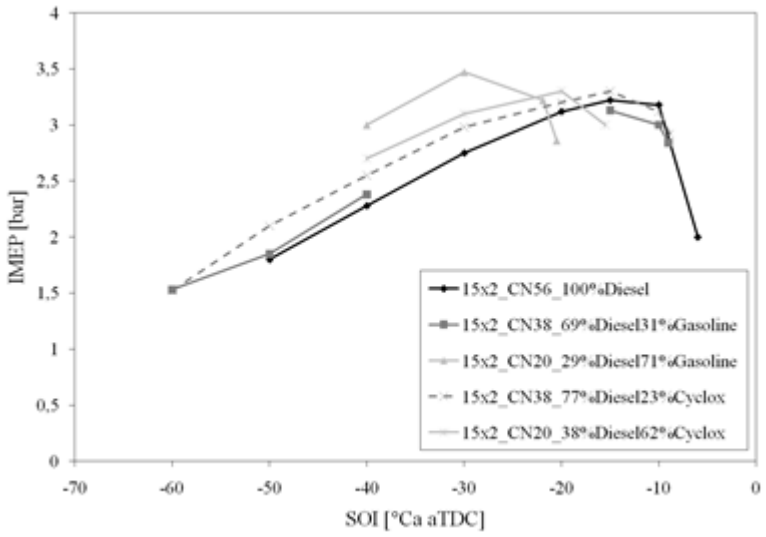


Figure 4.10: IMEP as function of SOI at 1500 rpm for all blends.

In Figure 4.11, the pressure rise rates for all blends are presented. The CN38 blends reach the 8.9 bar/ °Ca limit at similar SOI timings, which suggests they perform similarly.

For the CN20 blends, the longer ID creates more mixing time. This combined with the typical higher swirl level adopted in the LD engines (as in the present case), and the relatively low fuelling rate applied, increases to fuel over-mixing.

Obviously, as can be seen in Figure 4.11, the NOx trend is similar to the one that offers the pressure rise rate [4]. As it could be expected, the pressure rise rate determines the peak combustion temperature and therefore indirectly the NO_x emissions. Naturally, the lowest NO_x values are found for operating conditions where the pressure rise rate is low as well.

The CN38 blends show more or less the same trends as the reference fuel since the diesel fuel remain the main component. Lower NO_x values are emitted for the CN20 blends, due to the longer ignition delay that increases fuel-premixing level.

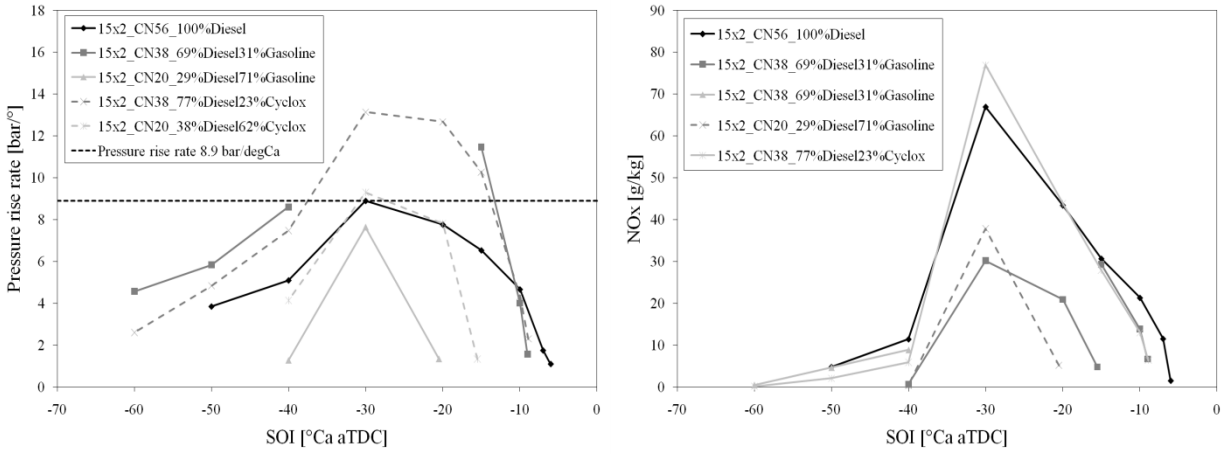


Figure 4.11: Pressure rise rate and NO_x emissions as a function of SOI at 1500 rpm for all blends.

Figure 4.12 shows the HC and CO trends. As discussed earlier, the lower CN blends (e.g. higher percentages of gasoline and CyclOx, CN20), mainly the gasoline blends, support the assumption that the over-lean phenomenon leads to more charge dilution and therefore lower temperatures and higher CO emissions.

In addition, here, the uncertainties pertaining the CN estimation (mainly for the CN20 blends) and the differences in terms of volatility are evident. In fact, such differences induce, for diesel/CyclOx, lower HC and CO emissions.

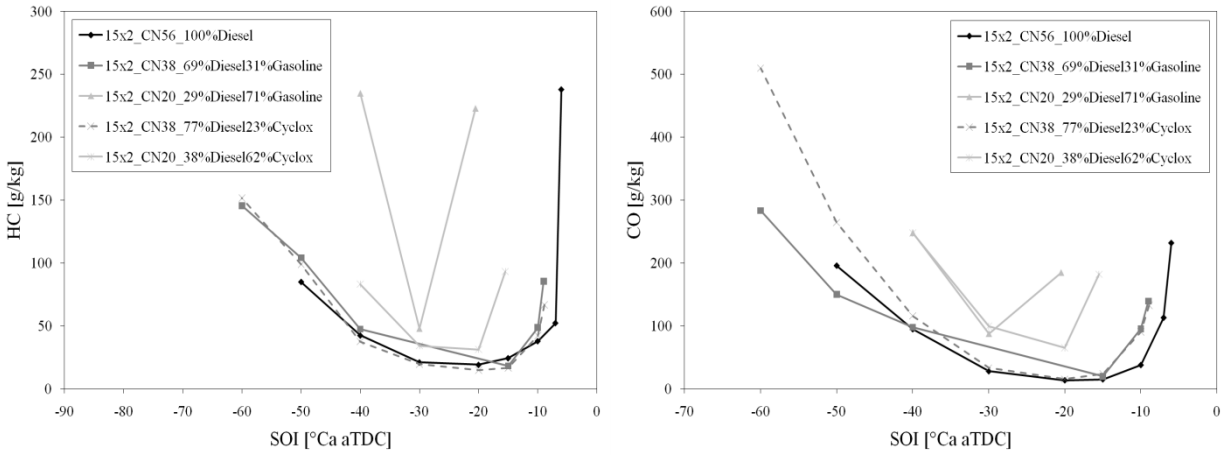


Figure 4.12: HC and CO emissions as a function of SOI at 1500 rpm for all blends.

The soot emissions reported in Figure 4.13(on the left) are extremely low (about 0.01 FSN) for these operating conditions. Accordingly, given the measurement uncertainly, no hard conclusions can be drawn. However, it appears that the lowest values are found for the lowest CN blends and in particular, the diesel/ CyclOx blend. This supports the assumption reported in [120][121] that high levels of premixing and higher percentages of oxygen are important drivers in suppressing soot emissions.

Figure 4.13(on the right) displays the ID as a function of the SOI. Both the CN38 blends show a similar characteristic. Of course, when CyclOx and gasoline become the main blend components (e.g. in CN20), the ID increases more. Looking at the two CN20 blends, due to its slightly lower CN and volatility, the gasoline blend shows higher ID values than those seen for the CyclOx blend. However, as discussed earlier, this trend may also be linked to higher HC emissions

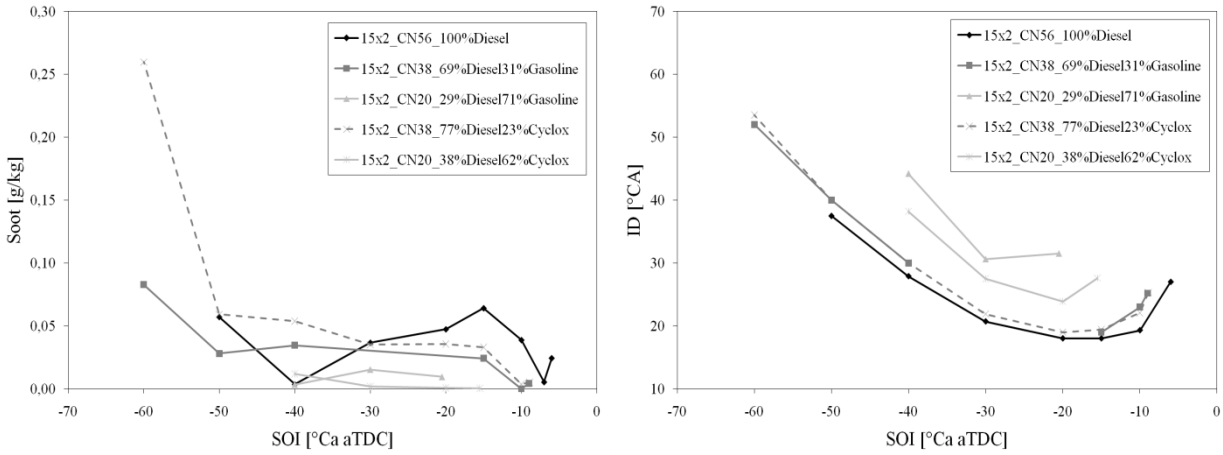


Figure 4.13: Soot emissions and Ignition delay as a function of SOI at 1500 rpm for all blends.

Engine performance analyses at constant injected energy flow at a fixed SOI

1500 rpm; IMEP= 3.2 bar-SOI= -40 °Ca aTDC

As stated before, it was not possible to perform the tests for all the SOI values for each blend, mainly for the blend 2. This was due to excessive pressure rise rates (Figure 4.11) or combustion instability. Accordingly, only the comparisons for SOI -40 °Ca aTDC are made.

This point simulate an early direct injection strategy (EDI) usually performed to achieve a PCCI combustion mode (see Chapter 2).

The figures report the pressure traces and RoHR, the thermodynamic temperature (Figure 4.14) and the emissions and efficiencies (Figure 4.15) for all blends at 1500 rpm. In each case, the SOI and injected energy is kept constant and equal to that of the reference point.

As could be expected, the MBF50% is retarded for the CN38 blends and the maximum peak is higher with respect to the reference diesel fuel (Figure 4.14). This difference is mainly due to a more efficient mixing process. Obviously, the CN20 blends show a more retarded start of combustion. The gasoline blend delays more the MBF50% and reduces the combustion temperature (Figure 4.14).

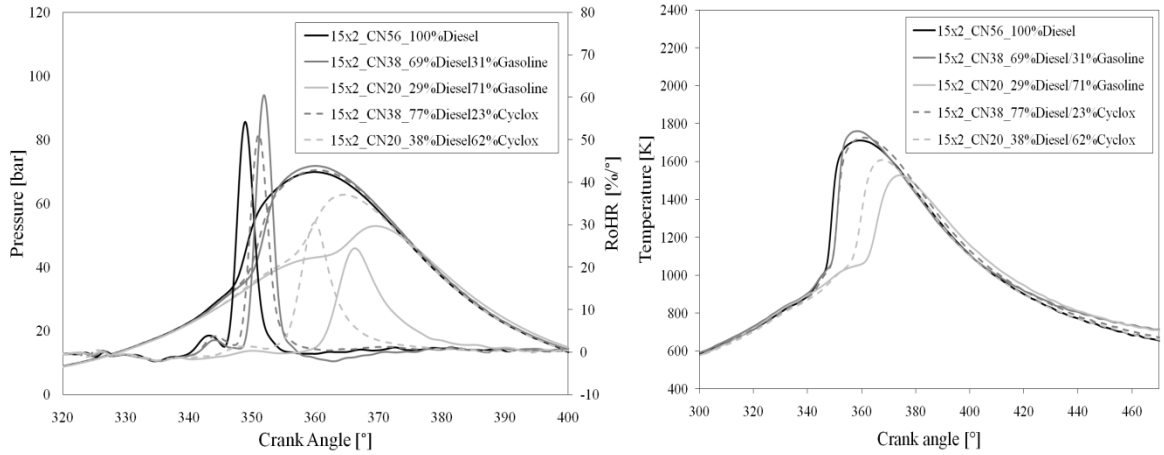


Figure 4.14: Pressure traces and RoHR (left) and the Thermodynamic temperature (right) for all blends at 1500 rpm, SOI -40 °Ca aTDC for the same injected energy.

The trends in terms of pressure and RoHR traces (Figure 4.14), the higher CO and lower NO_x emissions (Figure 4.15), are typical for a PCCI operating mode. The higher UHC emissions, as discussed earlier, are induced by over-mixing, wall wetting and out-of-bowl and crevice phenomena. These conclusions appear also valid for the CyclOx blend, despite the lower volatility and the presence of oxygen.

For the CN20 blends, very low levels of NO_x and high levels for CO are observed. This is explained partially by a decrease in the global temperature (Figure 4.14). However, the most important precursor for NO_x is not the global temperature but the local temperature. The lower CN for the CN20 blends induces more mixing time and therefore higher mixing rates inside the cylinder and a more homogeneous charge is developed. This limits the presence of thermal NO production zones.

The soot emissions were omitted for all the blends, because the exhaust concentration values were always low and at the limit of the measurement device.

In Figure 4.15, the fuel efficiencies and the ISFC are reported. They show similar values for ISFC for all the blends, whereas the combustion efficiency is obviously lower for the blends that emit more CO and HC. The thermodynamic efficiency for the low CN blends is higher due to the improved combustion phasing in the engine thermodynamic cycle. Actually, the lower CN blends show retarded combustion, which causes a better combustion phasing (MBF50%) and therefore higher thermodynamic efficiencies (see etha thermo in Figure 4.15). The combination

of the combustion and thermodynamic efficiency gives the fuel efficiency, which suggests that, for the low CN fuels, the lower combustion efficiency is compensated by improved combustion phasing.

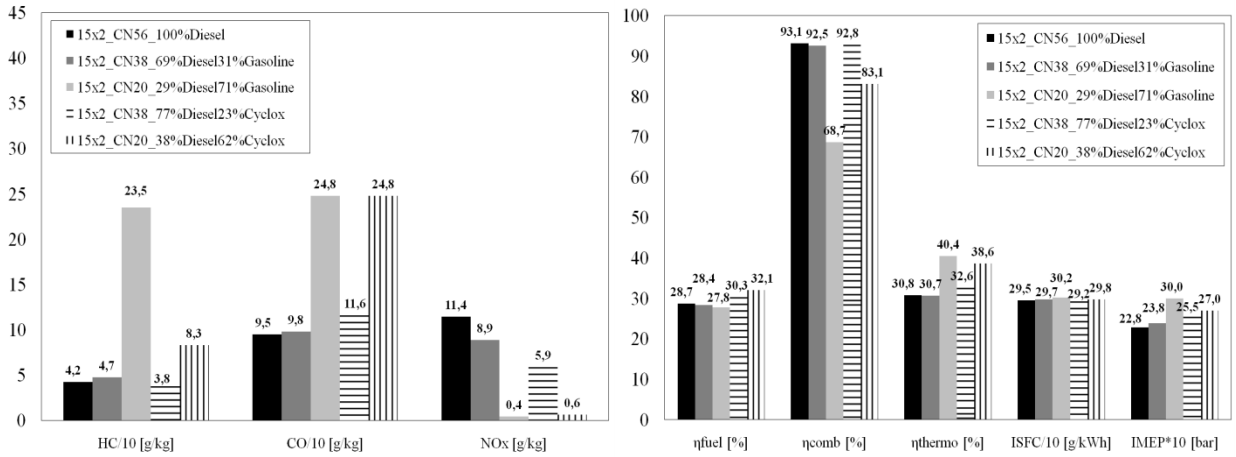


Figure 4.15: Emission Indices and efficiencies comparisons for all blends at 1500 rpm, SOI -40 °Ca aTDC for the same injected energy.

2000 rpm; IMEP= 6.9 bar

For higher speeds and loads, due to the limitations of maximum pressure rise rate, few workpoints were possible to perform. For each blend in terms of SOI (Figure 4.16), and therefore the operating range was smaller with respect to the low load conditions. This is mainly due to the higher amount of injected fuel which burns simultaneously and therefore causes higher pressure rise rates (see Figure 4.17, on the left) [104]. Indeed, for all the blends only a small SOI variation is permitted.

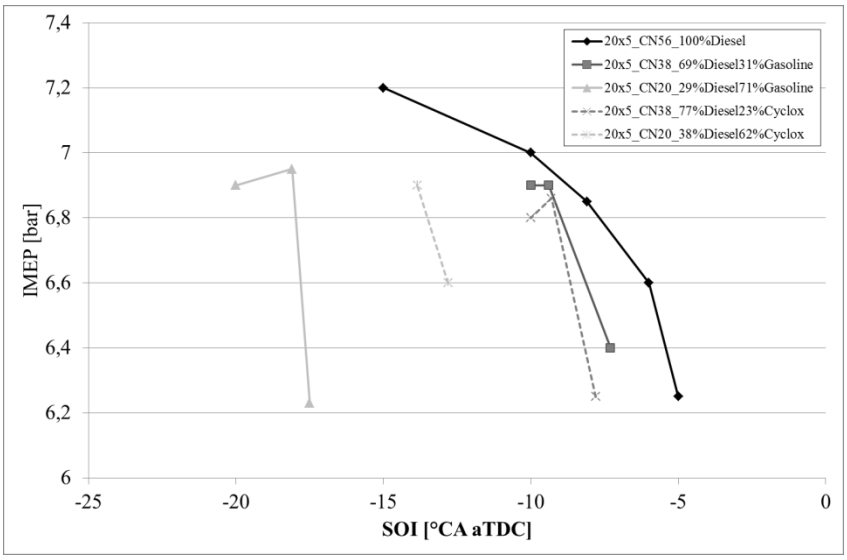


Figure 4.16: IMEP as function of SOI at 2000rpm for all the blends.

The pressure rise rate is dependent on the degree of mixing. It is higher due to the higher available amount of fuel to burn when the combustion starts. Like discussed before for 1500rpm, the emitted NOx is linked to the pressure rise rate and as expected the trends are similar to the ones for lower loads.

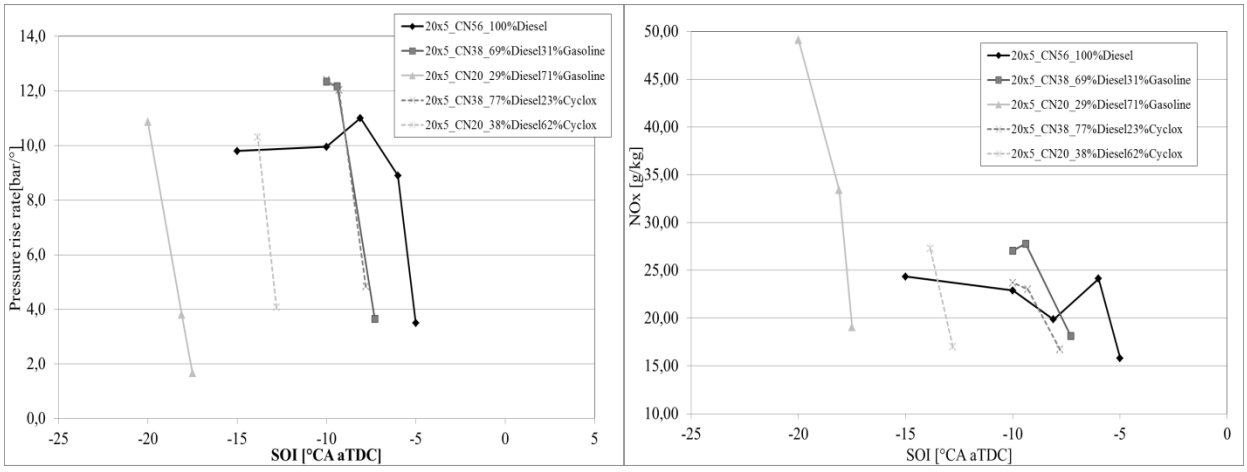


Figure 4.17: Pressure rise rate and NOx emissions as function of SOI at 2000rpm for all the blends.

The HC and CO emissions (Figure 4.18), for the fuels with CN38, are similar as the emissions for the reference points; whereas the CN20 blends show large differences due to the combustion instability. The CO emissions (Figure 4.18, on the right) are linked to the temperature and more.

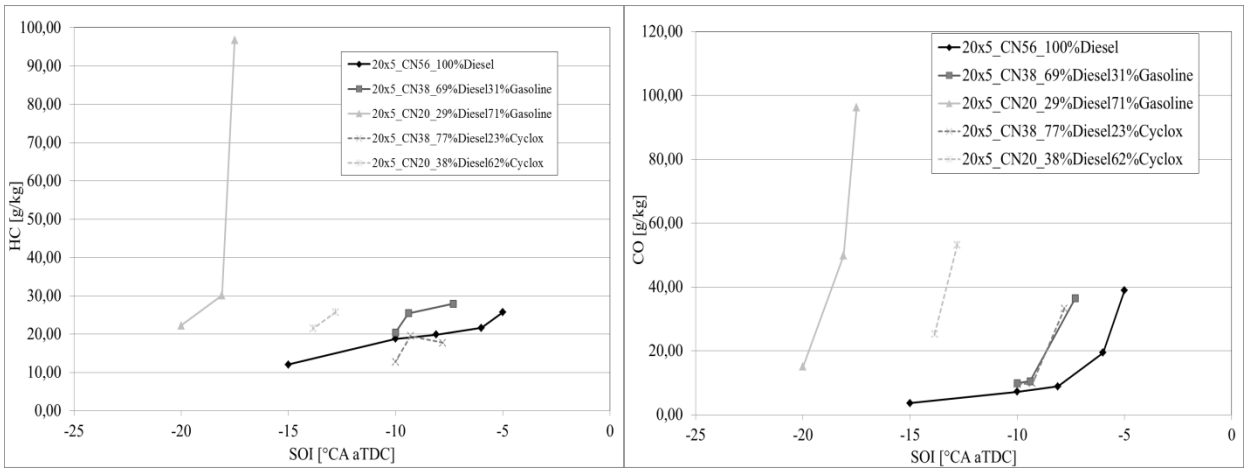


Figure 4.18: HC and CO emissions as function of SOI at 2000rpm for all the blends.

In Figure 4.19, on the left, are reported the soot emissions for all the blends. It is not possible to formulate hard conclusions based on these because of the limited SOI range, but it is possible to make some assumptions for the CN and/or oxygen effect on the soot emissions. In fact, the blend with cyclohexanone, especially the one with CN20, shows drastic soot reductions with respect to the other blends.

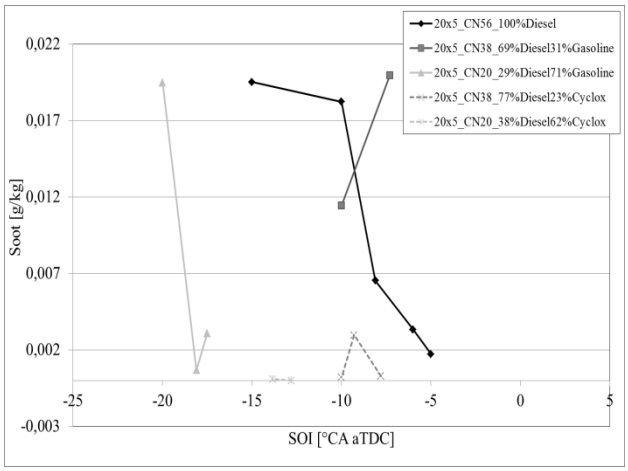


Figure 4.19: Soot emissions as function of SOI at 2000rpm for all the blends.

Engine performance analyses at constant injected energy flow at a fixed SOI

2000 rpm; IMEP= 6.9 bar_SOI= -10 °Ca aTDC

As described before, at 2000rpm it was not possible to perform test with CN20 blends so only comparisons between blends with CN38 are possible at SOI -10° (Figure 4.20).
The pressure traces are comparable for the three fuels therefore also HC and CO are at the same level. Moreover, even if the boiling curve for gasoline is more favourable for the mixing process, the level of smoke level for the diesel/cyclohexanone blend is much lower at similar NOx. This is attributable to the oxygen effect. This phenomenon is remarkable, also for the trade-off (next paragraph) where no total premixed conditions were realized (pilot + main). This confirms that, in such conditions, the oxygen content influences the soot reduction more than the CN.

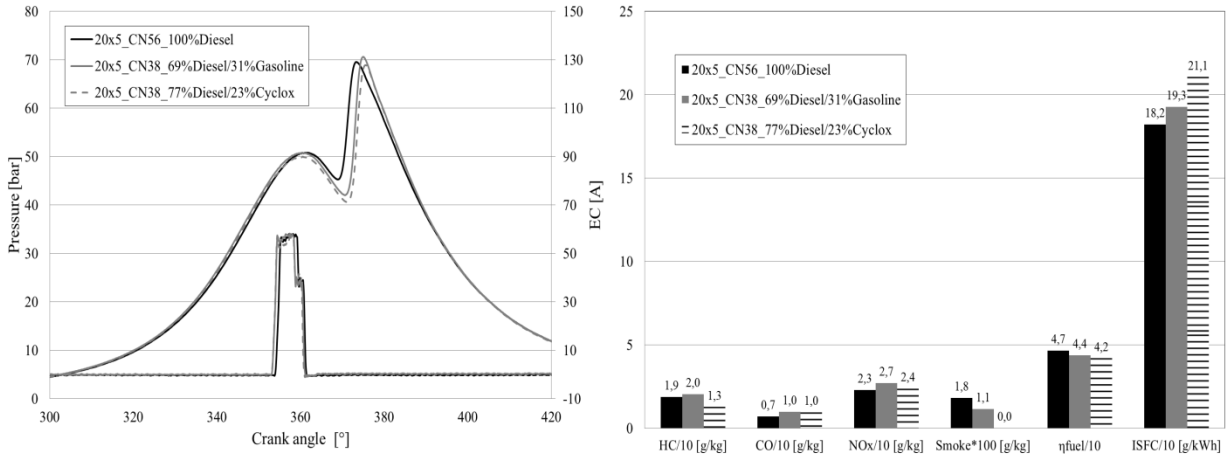


Figure 4.20: Pressure traces and energizing current (left), Emission Indices and efficiencies (right); comparisons diesel and blend with CN38 at 2000rpm, SOI -10° for the same injected energy.

4.5 EGR sweep with conventional diesel combustion

Trade-offs were performed because of their considerable importance due to the following considerations. The EGR is the main driver for NO_x emission control. To reach ultra-low NO_x emissions, high EGR rates are required. Accordingly, the premixed combustion contributes to

control the PM formation assisting simultaneously the EGR work for NO_x control because lower combustion temperatures can be attained. However, in some engine conditions, pilot injection could be necessary to control the combustion stability and the engine noise due to too high cylinder pressure rise rates. All combustion control measures for emission reduction have to be applying within absolute constraints on maximum fuel consumption and pressure rise (Table 4.4). Therefore, two test series where performed in order to evaluate the performance of the low CN fuels [22].

4.5.1 Experimental procedure

Starting from a reference Euro 5 calibration of real engines of similar characteristics, based on the use of moderate EGR levels, pilot plus main injection strategy and medium-high injection pressure, the fuel blends were analysed performing the conventional EGR trade-off at constant indicated mean effective pressure (IMEP). This was done until the cycle-to-cycle IMEP variability (up to 4% of the coefficient of variation – COV) or the exhaust smoke exceeded their prefixed limits (described later). Performing the trade-off, in order to avoid too high penalties in the engine thermodynamic efficiency, the MBF50% value was kept constant (its value depending on the engine test point, Table 4.3) varying the start of injection (SOI). In this way, the limits toward low NO_x emissions with conventional diesel operating mode of all fuel blends can be evaluated.
As stated before, the EGR sweep was performed in the two work points 1500x3.2 and 2000x6.9 starting from zero EGR, increasing the EGR rate.

4.5.2 Test Results

In the low speed and load point, i.e. 1500x3.2, the trade-off was plotted as CO vs. NO_x instead of soot vs. NO_x because, for modern engines, at low loads the CO emission becomes the main pollutant. The emissions are converted into specific emission indexes (EI) represented as g_{emiss}/kg_{fuel} units. The MBF50% values were 12° crank angle (CA) after top dead center (aTDC) for the test point 1500x3.2, and 15° CA aTDC for the test point 2000x6.9.

The Figure 4.21 and Figure 4.22 report the diagrams of CO, PM and UHC variation versus NO_x for the two considered test points.

In the diagrams, the measure uncertainty bars for the diesel (D) and the estimated "engine out" Euro 5 limits (Figure 4.21) are also reported. The limits are derived from engine complied Euro 5 targets, with a unit displacement similar to the single cylinder employed in the experiments.

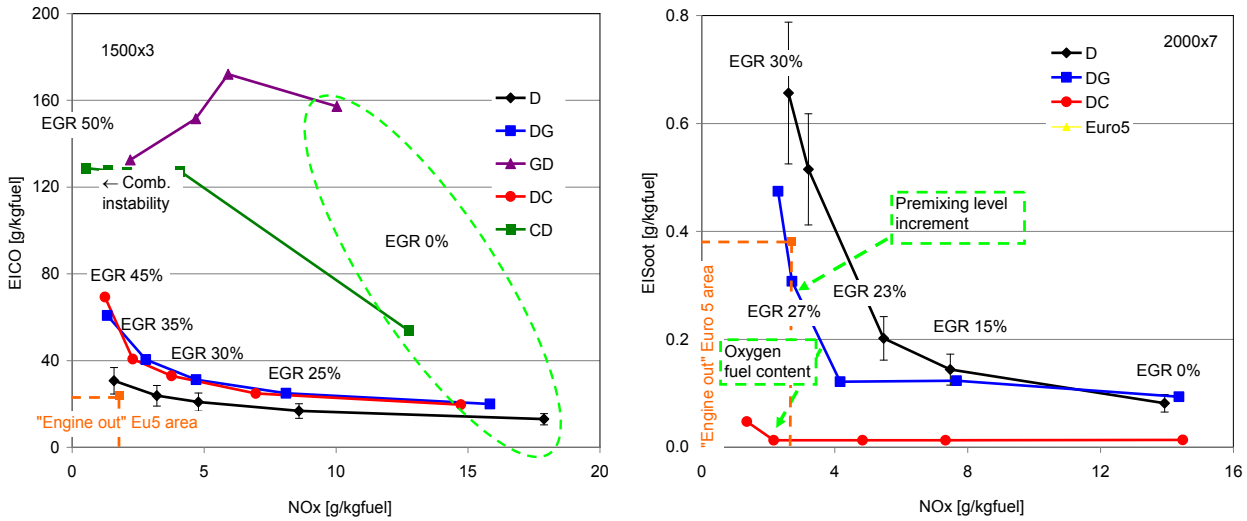


Figure 4.21: Trade off CO vs. NO_x at 1500x3.2 for all the blends (left); trade off PM vs. NO_x at 2000x6.9 for all the blends (right).

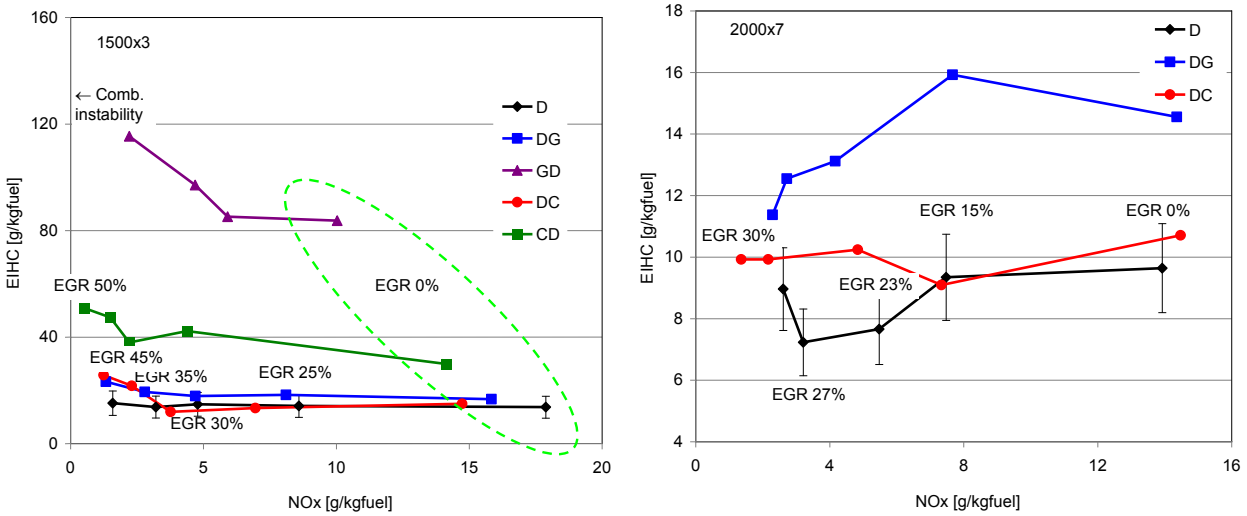


Figure 4.22: Trade off UHC vs. NO_x at 1500x3.2 (left), and at 2000x6.9 (right), for all the blends.

The first experimental evidence suggests that by reducing CN it is possible to improve the PM-NOx trade-off at medium load, well below the Euro5 limits, despite of an increment of CO-NOx

trade-off. At 2000x7, due to a high IMEP instability (COV up to 3.5%), tests with blends 4 and 5 (highest fraction of gasoline and CYCLOX in the blend) were not executed. These results are in line with previous experiences of other researchers [104][107][120]. In Figure 4.21 on the right, a PM-NO_x trade-off reduction is associated with an increment on ID time and therefore of the premixing time, while high CO emissions are associated with reduction of the local mixture strength toward the global in-cylinder very lean air-fuel ratio. Simultaneously, this effect leads to shift the flame temperature towards the thermodynamic bulk temperature and so to lower NO_x formation rates, as observable for data points corresponding to the test without EGR. A recent paper from Benajes *et al.* [124] discusses the local mixture distribution variation when gasoline is injected instead of diesel fuel.

On the left diagram of Figure 4.23 it is possible to note the limited EGR sweep of blend 3 (diesel in gasoline) with respect to the others, because of the combustion instability with an IMEP COV higher than 3.5%. The limited EGR sweep at the test point 1500x3.2 for the GD blend indicates that although a pilot injection is present, its effect on the auto-ignition stability of the main injection becomes ineffective at high EGR rate. Vice versa, at about the same CN level, less volatile fuels give better results in terms of combustion stability, even if CO emissions remain high. This result seems to conflict with those of Kalghatgi et al. [120] where for CN<30, the fuel volatility has less influence on combustion conditions. Considering the uncertainty on the actual CN of the present blends (determined with the linear Kay's mixing rule), and as showed later in the plot of the indicated signals, the large difference in SOImain between GD and CD, a discrepancy between the results of the two researches is acceptable.

The breakup of the PM-NO_x trade-off with EGR sweep for the DC fuel, plotted in the right diagram of Figure 4.21, is essentially due to the oxygen content of the CYCLOX. On the contrary, DG fuel shows similar PM emissions for moderate EGR levels, and gives better PM trend at higher EGR rate.

Figure 4.22, on the left, confirms the effect of CN reduction on UHC emissions. Nevertheless, it is important to highlight that the pilot drastically increases the UHC emissions in the whole EGR sweep and in both the two operating points when low CN fuels are employed. At 2000x7, the slight reduction for the DG blend increasing EGR is due to the predominant effect of exhaust flow reduction versus the UHC concentration increment. Of course, the pilot presence could be

useful to control ID and pressure rise in some operating conditions, but for low CN fuels, a too high degree of over-mixing is realized for very early pilot injection timings. This comment is well explained by the left diagram of Figure 4.23 where the SOI values for main and pilot are displayed. This means that whereas in the engine working map a pilot activation is necessary to control fuel ignitability and maximum pressure rise, nevertheless an accurate pilot injection management is required to burning low CN fuels (e.g. SOI pilot close to the main etc.) and also to avoid its over dispersion in the combustion chamber (and in the piston squish area) and as a consequence there are uncontrollable UHC emissions. The analysis of the influence of pilot injection parameters (e.g. quantity and dwell time) on combustion of low CN fuels was out of the aim of the present work, but it will be included in future studies. However, the improvement of pilot injection management, when it is required, seems mandatory when CN is reduced and fuel volatility increases. To do this, new injectors able to actuate the injection rate shaping could be useful. Indeed, the COV variation with EGR sweep reported in the right diagram of Figure 4.23 shows the significant rise of cycle-to-cycle variation of IMEP moving progressively from diesel (D) to gasoline and diesel (GD).

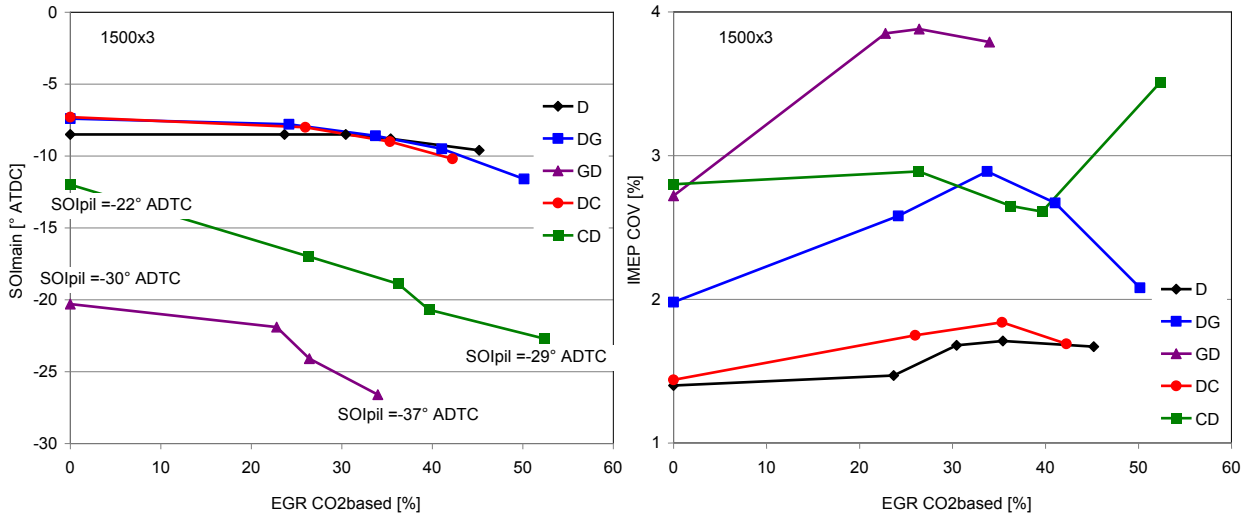


Figure 4.23: At left, SOImain variations for EGR sweep at 1500x3.2 for all the blends. SOIpilot of the two lowest CN fuels without EGR and for the highest EGR are also reported. At right, COV of IMEP with EGR sweep for all the blends.

The analysis of the combustion characteristics of all blends can be outlined looking at the plots of the indicated signals reported in Figure 4.24 for the test case 1500x3 and an average EGR rate

among all fuels of 37%, and in Figure 4.25 for the test case 2000x7 and an average EGR rate among all fuels of 28%.

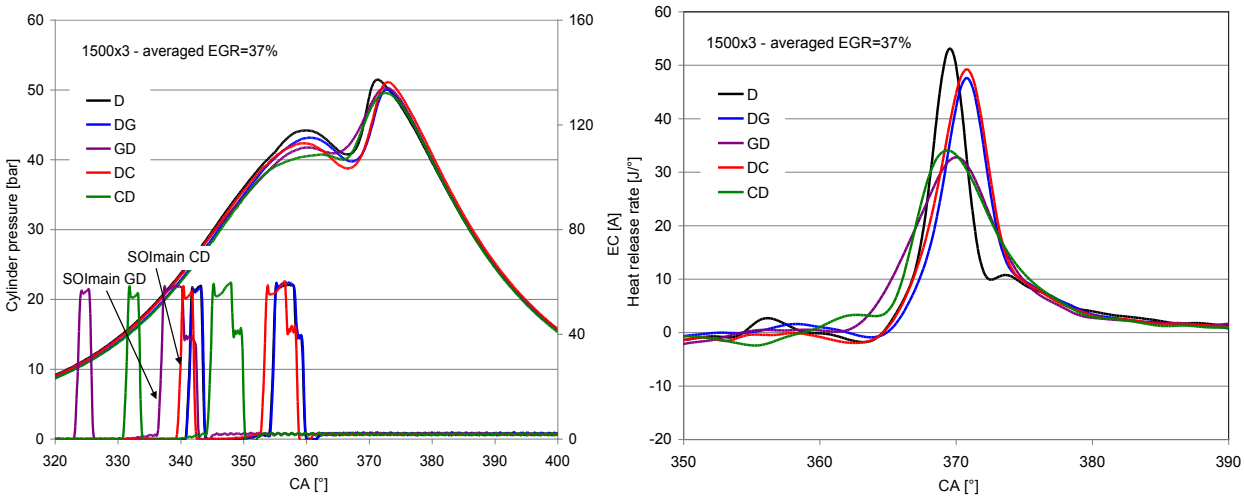


Figure 4.24: At left, cylinder pressure and injector energizing current versus crank angle; at right, heat release rate versus crank angle; curves of all blends are referred to the test case 1500x3.2 and with an EGR rate of 37%.

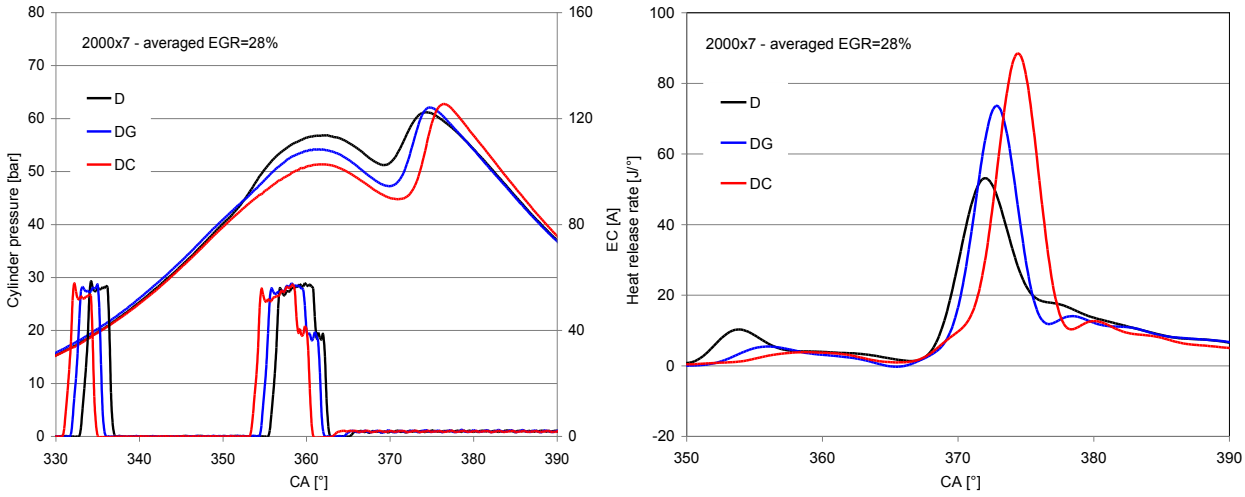


Figure 4.25: At left, cylinder pressure and injector energizing current versus crank angle; at right heat release rate versus crank angle; curves of all blends are referred to the test case 2000x6.9 and with an EGR rate of 28%.

At 1500x3 in Figure 4.24, starting from the diesel case (D), it is evident that the pilot combustion is visible and the combustion of the main injection shows the highest heat release rate. Moving toward lower CN blends, SOImain has to be advanced progressively in the

compression stroke, pilot combustion reduces its effectiveness and for lowest CN blends, combustion approaches the typical HCCI shape, indicating that pilot has a negligible or weak influence on ignition. This is valid for both the CYCLOX and gasoline blends, and this data is in line with the emission results of Figure 4.21 and Figure 4.22. This trend is also visible in the diagrams of Figure 4.25, for the test point 2000x7. In the present test case, the difference in SOImain between DG and DC blend is attributable to the lower LHV of the DC blend that gives less heat released from pilot combustion. Such an effect is notable also in Figure 4.24 for the heat release rate (HRR) traces of the DG and DC blends.

The excessive over-mixing phenomenon for reducing CN is the main factor that affects the ISFC increment and the relative indicated thermal efficiency. This trend is for both test points and all blends displayed in Figure 4.26 and Figure 4.27 for ISFC and thermal efficiency respectively.

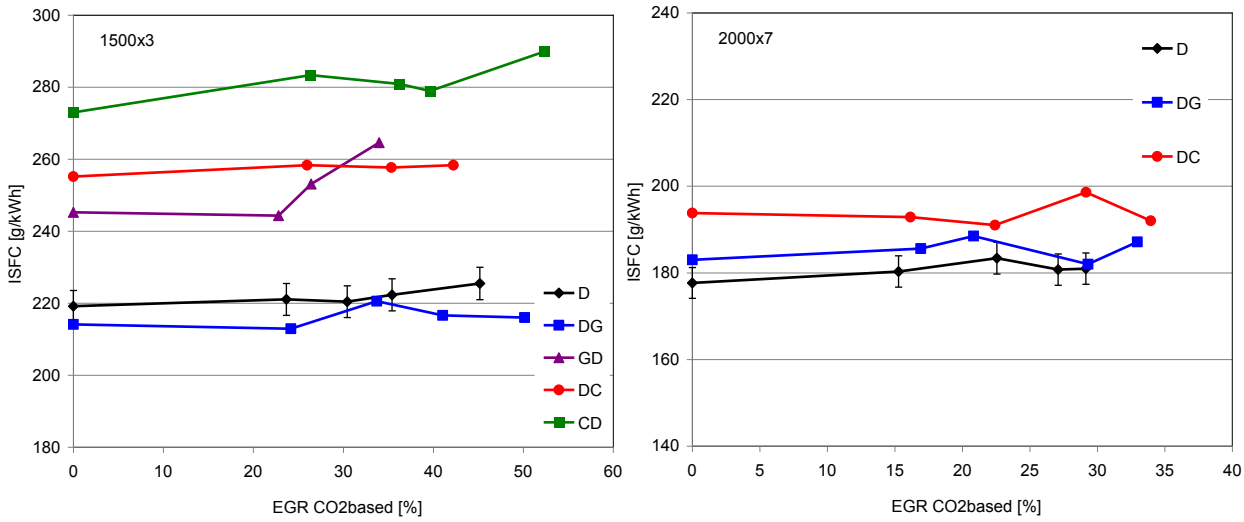


Figure 4.26: ISFC variations for EGR sweep at 1500x3.2 (left) and at 2000x6.9 (right) for all the blends.

The diagrams show quite "flat" trends versus the EGR, except for the highest rates where an ISFC rise is generally expected. These trends seem different from the results found by Kalghatgi *et al*. [120] in similar tests and for similar fuels. Actually, in other test series performing the SOI sweep of a single injection event per cycle with and without EGR, the authors found a slight reduction of ISFC for the EGR case with respect to the zero EGR case. Therefore, in line with other literature data ([120][125]), the ISFC insensibility to EGR may be attributed to the

presence of a pilot injection that progressively reduces the combustion efficiency as the SOImain is advanced to keep the MBF50% timing constant. The effect is clearly visible in the ISFC trend of the GD blend at 1500x3.2. In that case, the ISFC rise was detected for low EGR rate (20%). The corresponding indicated signals of the GD blend in Figure 4.24 denotes the very early timing of SOIpilot that, pointed out before, loses its effectiveness reducing combustion efficiency and increasing the unburned emissions.

The trends of the indicated thermal efficiency for both test points and all blends reflect the trends for ISFC.

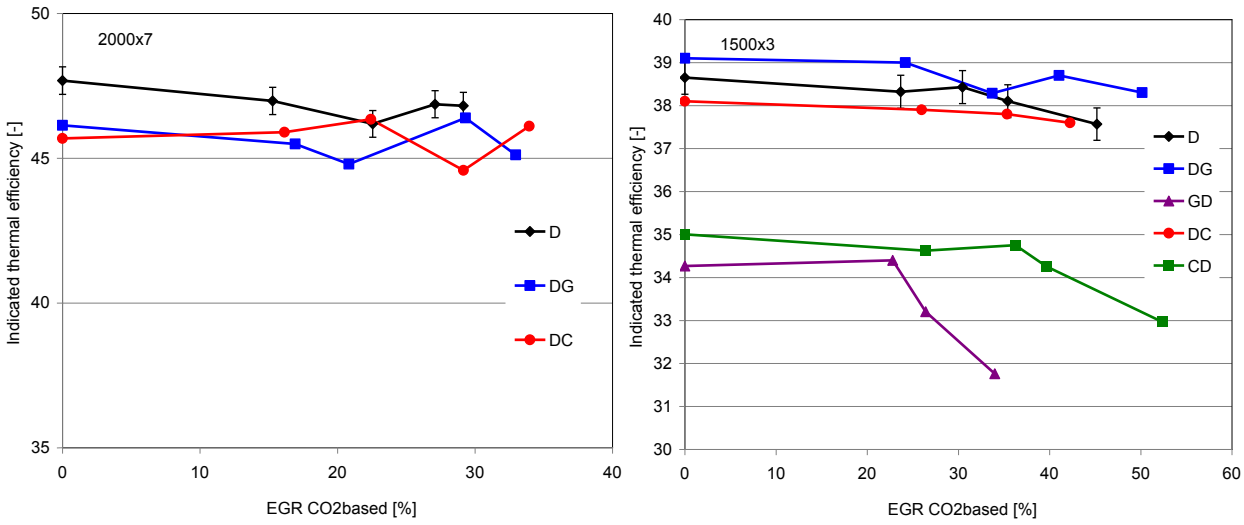


Figure 4.27: At left, Indicated thermal efficiency variations for EGR sweep at 1500x3.2 (on the left) and at 2000x6.9 (on the right) for all the blends.

The overall analysis of the experimental data of the diesel, gasoline and CYCLOX blends reported in the previous Figures points out the importance of the fuel characteristics to realize the combustion control when low CN fuels are burnt and a pilot and main injection is required to stabilize the combustion, limit the pressure rise rate and reduce emissions. The relevance is also highlighted in the plots of Figure 4.28. The plot on the left denotes the effectiveness of the pilot injection on COV and pressure rise rate value for the DG blend, while the right plot evidences the difficulties in the IMEP COV control when gasoline is the main component of the blend and the SOImain has to be advanced earlier in the compression stroke to have acceptable MBF50% values.

In this latter case (see right diagram of Figure 4.28), despite of quite similar ignition timing, and injection pressure variation inside the injector chamber, between the maximum and minimum IMEP cycle (see HRR traces), the combustion instability lies mainly on heat release of main injection, indicating a large variation of spray-air mixing and over-mixing of the main injection (in line with the results exposed in [124]). For similar test conditions as in the right diagram but without pilot activation, the COV was higher than 6%.

Therefore, in the comparison between a high quality gasoline and a less volatile low CN oxy-fuel, as CYCLOX, an evidenced improvement of the engine stability, unburned and PM emissions at the same NO_x exhaust level can be obtained with the second one, for those engine operating conditions (e.g. transient, cold starting etc.) where a pilot combustion is required to the combustion control. Similar results for a heavy-duty engine fed with the same kind of oxy-fuels can be found in [126]

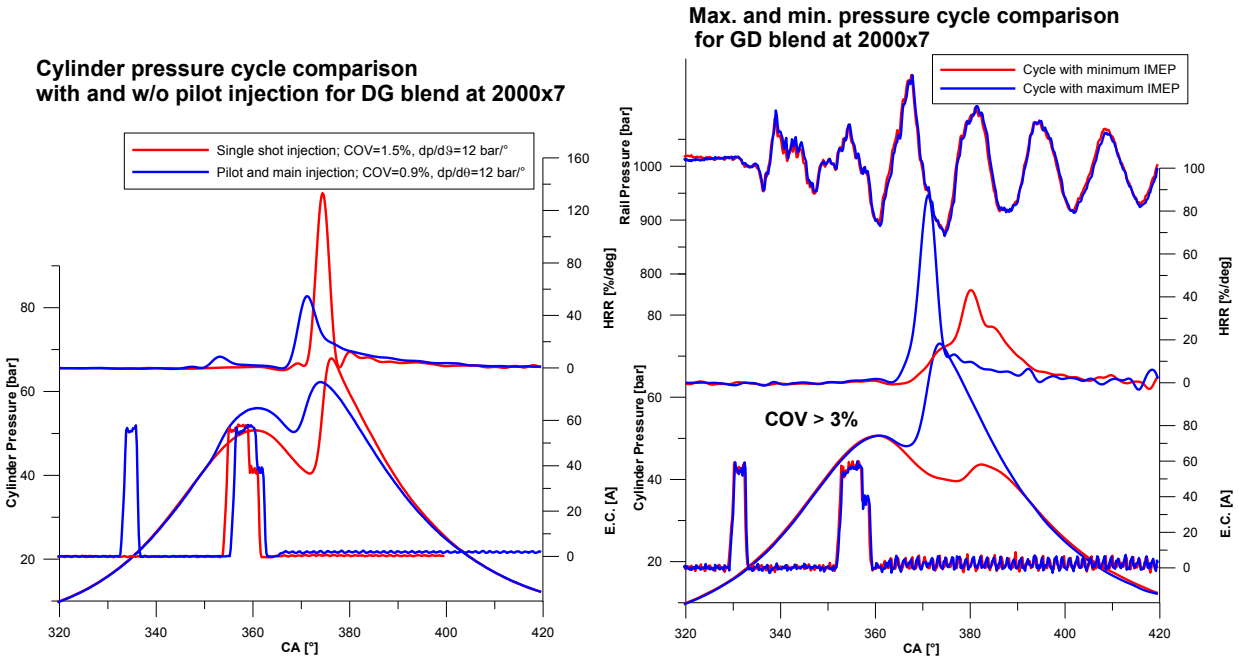


Figure 4.28: At left, indicated signal comparison for tests with and without pilot injection at 2000x6.9 for DG blend. At right, indicated signal comparison for cycles with maximum and minimum IMEP for the test with GD blend at 2000x6.9 and pilot plus main injection strategy.

4.6 PCCI application with low CN fuels

This paragraph has the aim at evaluating the lowest possible NO_x emission conditions in PCCI mode for the different fuels. The test methodology is hereby described.

4.6.1 Experimental procedure

PCCI operating mode is realized with a single injection event, increasing the EGR systematically, until one of the limits on the maximum values on fuel consumption, pressure rise and smoke emission is reached. In addition, in this case SOI was varied in order to keep the MBF50% constant. Even though very early, multiple injection strategies could be useful to realize well-premixed air-fuel charges [112], they were not considered in the present study because they require optimization of many parameters in each test point, as the dwell times among all injection events, the different quantities and so on. Moreover, the use of sophisticated injection strategies could affect the interpretation of the results. With this testing methodology the capability of the different blends (and fuels) to reduce NO_x in PCCI combustion mode within reasonable limits in efficiency, comfort and emissions, and for a fixed combustion system design (e.g. compression ratio, injection system characteristics and so on), can be evaluated. No limits on engine-out UHC and CO emissions were fixed since they were object of analysis of the quality of the fuels.
In the test series, injection pressure, boost pressure, exhaust backpressure, swirl level, intake air temperature and water coolant temperature were kept equal to the reference Euro 5 calibration.

4.6.2 Test results

In the present case, all four tests points were object of investigation. However, for the lowest CN blends (e.g. GD and CD), the IMEP variability and the cylinder pressure rise rate was always above the fixed limits for reliable functionality of the engine. For the CD blend, it was only possible to perform the tests at 1500x3.2 and 2000x6.9. For this reason, no data for the GD blend is displayed in the following.

Figure 4.29 shows some engine operating parameters and exhaust emissions for the blends for which it was possible to reach PCCI conditions at 1500x3.2. To show all the emission data in the same graph without normalization of the values, the different species emissions were properly scaled.

Considering the left diagram, the low value for IMEP for the DG blend is obvious. For this case, difficulties in controlling the combustion stability were observed with a slight reduction for the averaged IMEP consequently. Nevertheless, for the other fuels the target value for IMEP of 3.2bar was attained. From a first perspective, looking at the diagrams in Figure 4.29, it appears that PCCI conditions can be realized for all fuels within the prescribed limits. In this operating condition, it is quite easy to reach very low NO_x and low PM emission at high EGR rates. Nevertheless, both DG (with a CN ≈38) and CD blend (with a CN ≈20) yield very high-unburnt emissions.

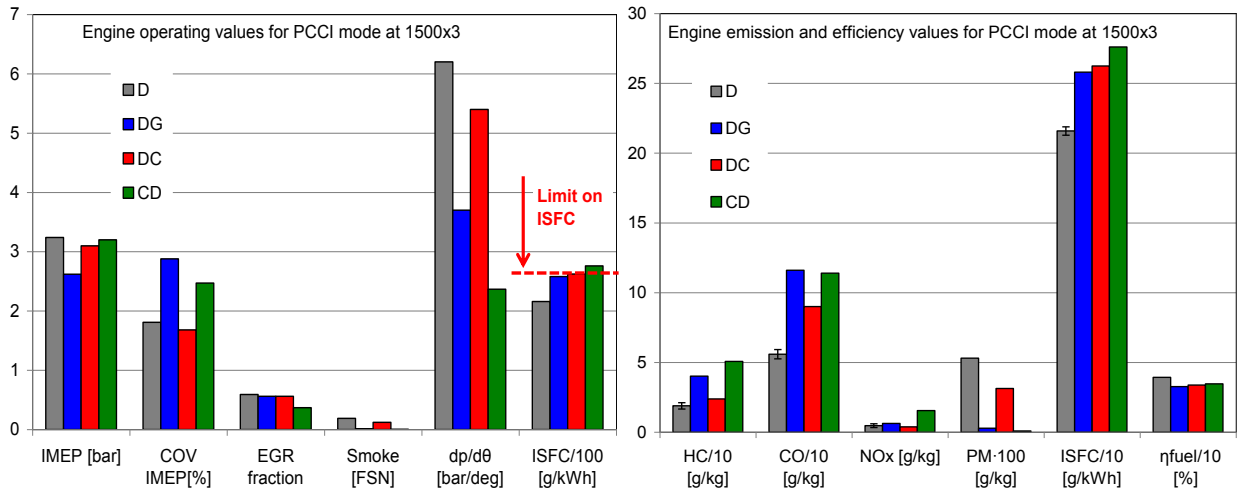


Figure 4.29: Engine operating parameters (left) and exhaust emissions (right) for all blends at the lowest attainable NOx emissions in PCCI conditions at 1500x3.2. Note that dp/dθ limit at 1500 rpm was fixed at 8.8 bar/°.

Figure 4.30, Figure 4.31 and Figure 4.32 report the same data of Figure 4.29 for the test points 1500x6.9, 2000x3.2 and 2000x6.9 respectively.

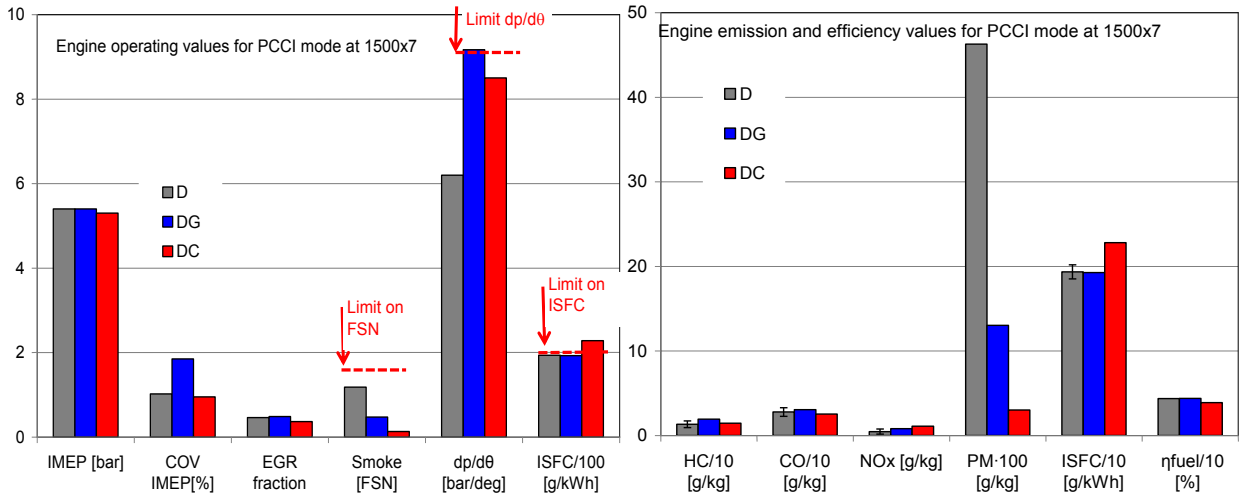


Figure 4.30: Engine operating parameters (left) and exhaust emissions (right) for all blends at the lowest attainable NOx emissions in PCCI conditions at 1500x6.9. Note that dp/dθ limit at 2000 rpm was fixed at 8.8 bar/°.

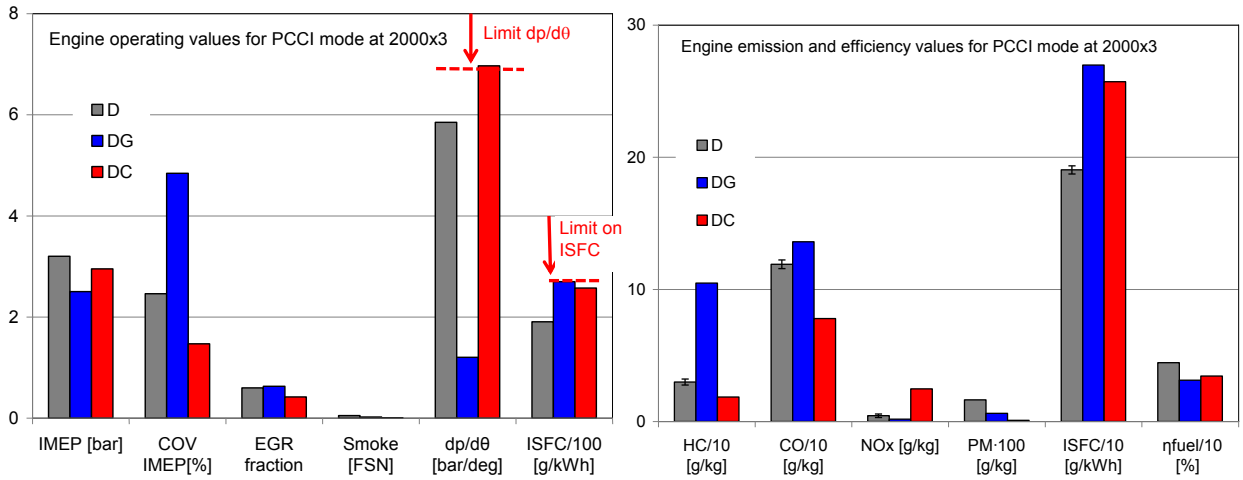


Figure 4.31: Engine operating parameters (left) and exhaust emissions (right) for all blends at the lowest attainable NOx emissions in PCCI conditions at 2000x3.2. Note that dp/dθ limit at 2000 rpm was fixed at 6.8 bar/°.

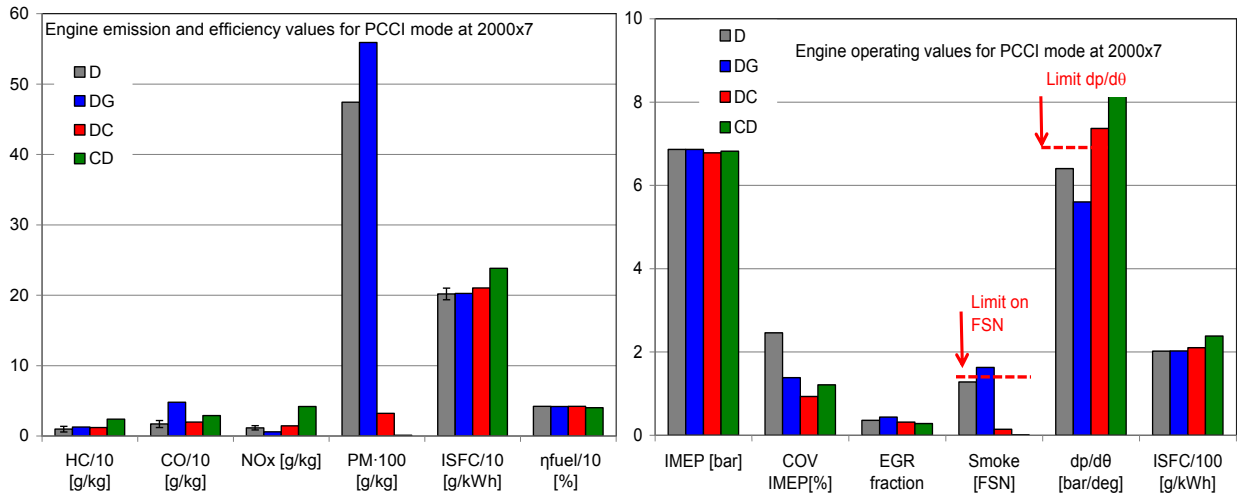


Figure 4.32: Engine operating parameters (left) and exhaust emissions (right) for all blends at the lowest attainable NOx emissions in PCCI conditions at 2000x6.9. Note that dp/dθ limit at 2000 rpm was fixed at 6.8 bar/°.

The data reported in the above figures point out that at low loads, ISFC and cylinder pressure rise rates are the limiting factors, while at medium loads, excessive smoke emissions and cylinder pressure rise rates limit the maximum EGR. In all the test points, very low NO_x emissions are reached with reasonable fuel consumption values. It is important to note that in all test points, the attained low NO_x emissions were very close to the exhaust levels required, in the corresponding operating point, by a four-cylinder engine to meet EURO 6 limits on the NEDC homologation procedure.

In this framework, the fuel characteristics have a great importance on the emissions. Indeed, looking in more detail at the operating parameters and the emission data in all the above Figures, the results suggest that for moderate fractions of low CN fuels in diesel, DG blend has a larger IMEP COV and CO emissions than DC, and at medium loads where COV is similar (e.g. 2000x6.9 in Figure 4.32), DG blend has a higher exhaust smoke level than DC and similar to the neat diesel (D). These last results are in agreement with data from Kalghatgi *et al*., where for medium loads and high EGR rates, gasoline gives similar soot emissions as diesel fuel. On the other hand, it is known that due to the high aromatic content of gasoline (see Table 4.2), its sooting tendency under rich fuel-air ratios is quite high. The highest soot emission level was observed for the DG blend, despite its longest premixing time and the lowest boiling curve with

respect to the D and DC blends. Figure 4.33, where cylinder pressure curves and injector energizing time traces are displayed for the test case 2000x6.9, shows the relative differences.

On the contrary, the DC blend shows overall better performance than the D and DG blend. Therefore, it can be noted that in PCCI combustion mode, at about the same CN as DG, the use of a less volatile oxygenated fuel gives more benefits on the in-cylinder air-fuel mixing preparation and soot formation suppression than the gasoline based blends.

In case of the lowest CN blends, as stated before, it was only possible to test the CD fuel at 1500x3.2 and 2000x6.9, while at 1500x5 and 2000x2, as for GD, too high combustion instability was observed.

As notable in Figure 4.29 and Figure 4.32, acceptable combustion stability for CD was attained for lower EGR values than the others fuels. This condition implies higher NO_x emissions and higher in-cylinder dp/dθ maximum values (see green bars in Figure 4.32), also despite of the long premixing times (see green curves in Figure 4.33). Moreover, this result highlights, also for low CN fuels, the clear link between air-fuel mixing conditions and combustion stability when the engine operates in PCCI mode and with high EGR rates.

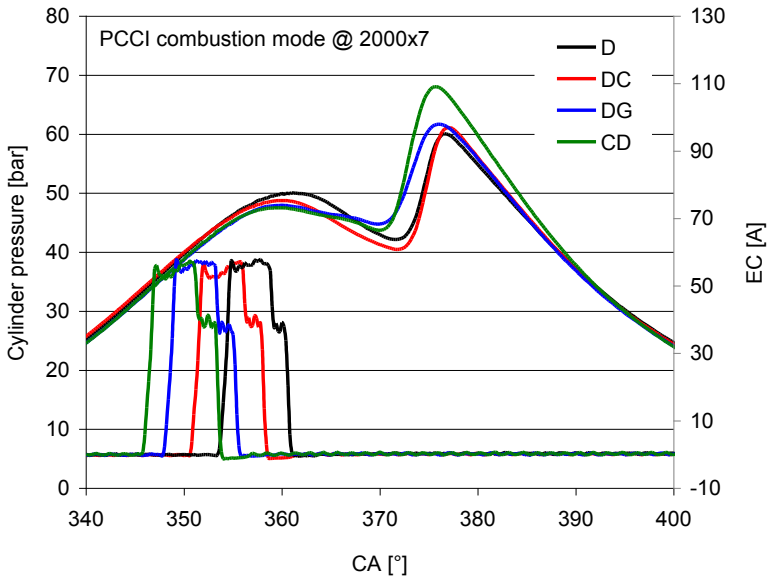


Figure 4.33: Cylinder pressure and injector energizing current versus crank angle of all tested blends in PCCI mode at 2000x6.9.

From this point of view, and based on the type of work performed by Benajes *et al.* in [124], it will be very interesting in future research to evaluate the critical mixing conditions versus characteristics of low CN fuels, where both the cycle-to-cycle combustion stability and unburnt emissions become unacceptable.

4.7 Nanoparticle emission from low CN oxy-fuels

Referring to the upcoming legislation in terms of number of nanoparticles (paragraph 1.1.2), measurements in terms of size and number of particle emissions was performed.
The aim was to assess the effect of the low oxy-fuels on the size distribution of the emitted nanoparticle. Diesel and DC fuel (Table 4.2) were compared either in PCCI (single injection) combustion mode either in conventional combustion mode (splitted injection).

4.7.1 PCCI combustion mode

In PCCI combustion mode, the tests were performed at 2000rpm and 5bar BMEP, which represent one of the most significant test points in terms of emissions (Figure 4.2). Two different EGR levels were adopted. The results are compared to the conventional combustion mode performed with pilot and main injection in order to assess the different distribution characteristics.
In Table 4.5 are reported the main engine parameters used fixed for this test campaign.

Fuel	Description	RPM	BMEP [bar]	SOI [Ca aTDC]	Δt_pil [µs]	Swirl [%]	P inj [bar]	EGR [%]	Smoke [mg/m3]
Diesel	PCCI	2000	5	-8	/	30	974	0	0.26
	PCC2	2000	5	-9	/	30	974	25	0.57
	Conventional	2000	5	-8	1524	30	974	19	3.35
DC	PCCI	2000	5	-10	/	30	974	0	0.02
	PCCI2	2000	5	-12	/	30	974	43	0.05
	Conventional	2000	5	-9	1524	30	974	22	0.5

Table 4.5: Main engine parameters in PCCI and conventional injection strategies.

In Figure 4.34 are reported the particle size distribution function (PSDF) measured for conventional combustion and premixed modes for both the tested fuels.

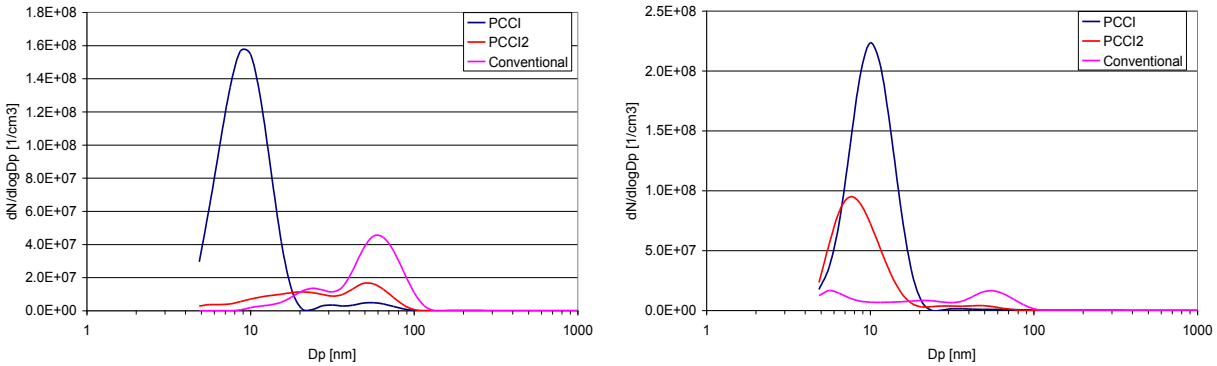


Figure 4.34: PDSF in conventional and PCCI mode with and without EGR for diesel (left) and for DC (right).

PSDFs show a bimodal size distribution both for premixed and conventional combustion modes. For both fuels, PCCI and PCCI2 modes show a strong reduction of particles larger than 20 nm. Moreover, the PCCI combustion shows a stronger nucleation mode (Figure 1.9) centred on around 10nm and an accumulation mode lower of around one order of magnitude compared to the conventional combustion mode. The nuclei mode is associated with the low amount of accumulation particles. This is consistent with the hypothesis of Kittelson *et al.* [127], who consider that nucleation is favoured by low accumulation mode particle number, due to the low adsorption of volatiles that can take place on the carbonaceous particles surface at these conditions. In fact, for diesel fuel, this result is only evident in PCCI combustion mode. As higher amount of EGR are used (PCCI2) larger amount of particles formed compared to PCCI even if they remain lower than in conventional mode. For DC fuel, a strong nucleation mode is observed for both PCCI and PCCI2 as the low accumulation mode.

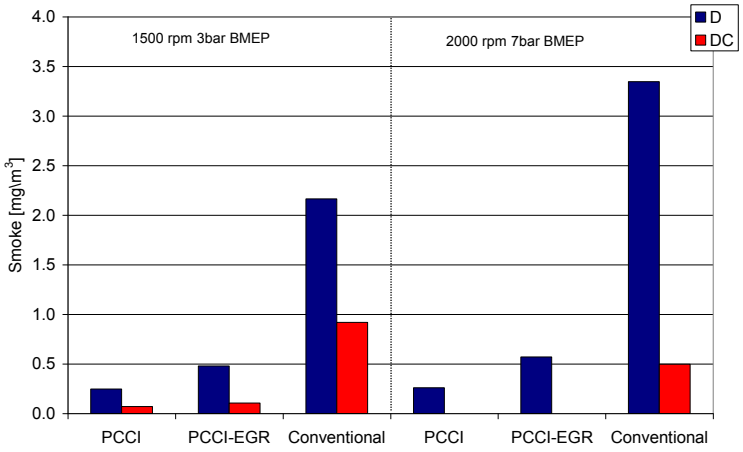


Figure 4.35: Smoke concentration comparison for the different strategies.

As stated in the previous paragraphs, DC blend show, in addition to smoke reduction (Figure 4.35), a significant advantage in terms of particle number emission. In fact, the future legislation computes the emitted particle number for particle with a diameter greater than about 20nm.

4.7.2 Conventional combustion mode

In conventional combustion mode, the tests were carried out in the reference points reported in Figure 4.36.

Test point[14]	RPM [1/min]	IMEP [bar]	BMEP [bar]	MBF50% [CA]
1500x3(2)	1500	3.2	2	12
2000x7(5)	2000	6.9	5	15

Figure 4.36: Reference test points.

Applying the conventional injection strategy, the experiments were performed both with and without EGR. The measurements without EGR allowed a comprehensive analysis of the fuel effect on the particle emissions. On the other hand, the tests with EGR are performed to analyse the effect of DC using the actual engine calibration. Moreover, at 2000rpm and 5bar BMEP and

[14] The values inside the parenthesis are referred to the BMEP value. The graphs that follows, sometimes refer to IMEP other times to BMEP(i.e. 1500x2 or 1500x3).

higher EGR rate of was applied in order to assess the effect using a EURO6-NOx reduction calibration strategy. In Table 4.6 are reported the main engine parameters.

Fuel	Description	RPM	BMEP [bar]	SOI [Ca aTDC]	Δt_pil [µs]	Swirl [%]	P inj	EGR [%]	Smoke [mg/m3]
Diesel	Pilot-Main-EGR0	1500	2	-8	1174	65	480	0	2.54
	Pilot-Main-EGR_map	1500	2	-8	1174	65	480	22	2.11
Diesel	Pilot-Main-EGR0	2000	5	-7	1524	30	974	0	1.57
	Pilot-Main-EGR_map	2000	5	-8	1524	30	974	21	4.35
	Pilot-Main-EGR2	2000	5	-8	1524	30	974	19	3.35
DC	Pilot-Main-EGR0	1500	2	-8	1174	65	480	0	1.65
	Pilot-Main-EGR_map	1500	2	-8	1174	65	480	25	0.9
DC	Pilot-Main-EGR0	2000	5	-8	1524	30	974	0	0.42
	Pilot-Main-EGRmap	2000	5	-9	1524	30	974	22	0.5
	Pilot-Main-EGR2	2000	5	-9	1524	30	974	16	0.5

Table 4.6: Main engine parameters in conventional injection strategies.

Figure 4.37 depicts the PSDF measured for D and DC engine fuelling at 1500rpm 3bar BMEP and EGR0 and EGR1.

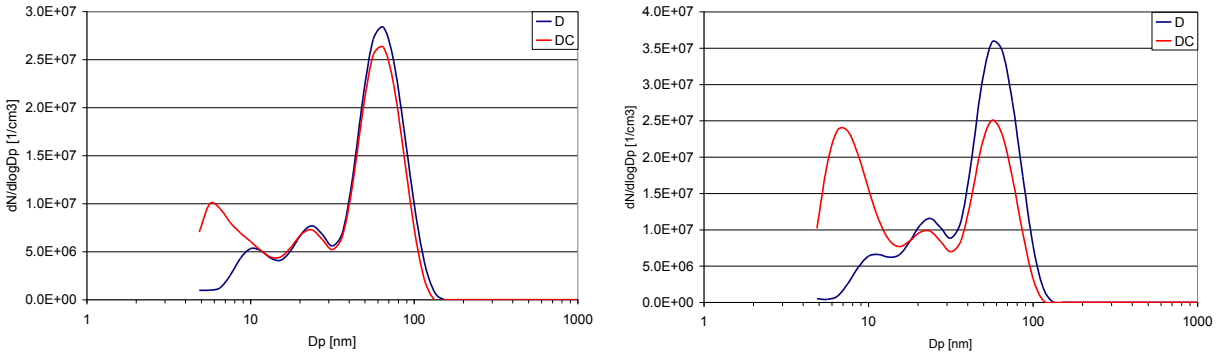


Figure 4.37: Particle size distribution measured for D and DC fuels at 1500rpm 3.2bar BMEP applying the pilot plus main injection strategy at EGR0 (left) and EGR1 (right).

For each fuel and for each condition are well resolvable three modes: the first peaked on 10nm, the second on 20nm and the third on 60nm. Fuelling DC, it is observed a larger number of

particles smaller than 10nm. On the other hand, the concentrations of particles larger than about 10 nm are reduced. These results are ascribable to a combination of several factors. In particular, the retarded combustion timing due to the low CN allows a better mixing reducing the formation of local rich zone in the combustion chamber. Moreover, the higher oxygen content and the higher soot reactivity favour particles oxidation [129][130][131].

Similar trends are observed at 2000rpm 5bar BMEP, as shown in Figure 4.38.

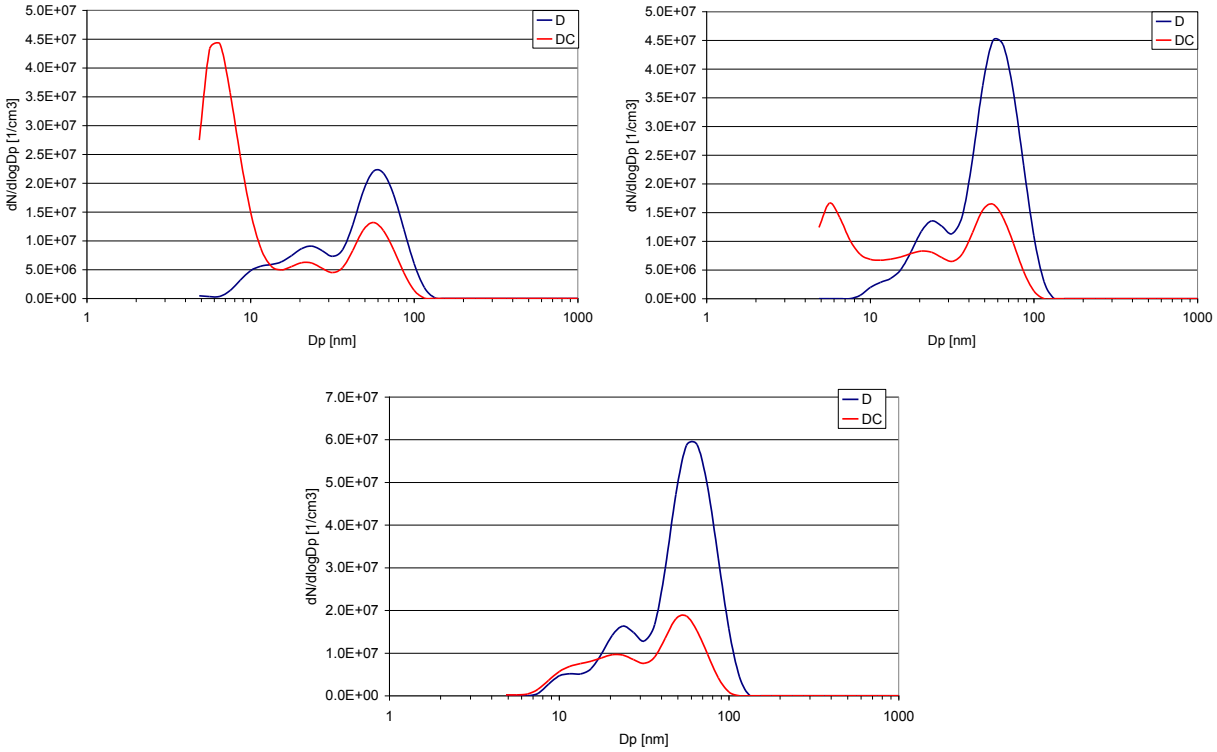


Figure 4.38: Particle size distribution measured for D and DC fuels at 2000rpm 6.9bar BMEP at EGR0 (left) and EGR1 (right) and EGR2 (bottom).

Looking at the diagrams reported in Figure 4.38, it is possible to observe the effects of the EGR on particle emissions. In particular, increasing the EGR rate, the particles smaller than 10nm decreases conversely the particle larger than 10nm increases. These results are in agreement with previous studies [127][128] that correlate the reduction of 10nm particles with the increase of the accumulation mode, as the adsorption or condensation of volatile materials on the particles surface prevails over the nucleation rate. Nonetheless, the effect of the EGR is less strong for DC fuel with respect to the diesel fuel. In particular, the number of the particle slightly increases passing from EGR0, EGR1 and EGR2. On the other hand, for diesel fuel the

particle number measured for EGR1 is quite the double than for EGR0. This result suggests higher EGR rate calibration can be used of oxygenated and low CN fuel allowing the reduction of the NOx emission without great particle emissions penalty.

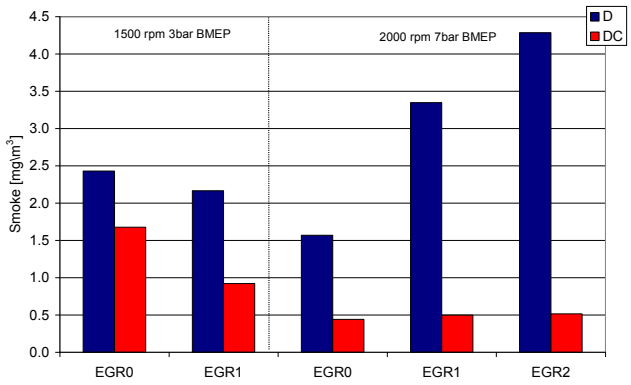


Figure 4.39: Smoke emissions at different EGR levels.

4.8 Conclusions

In this chapter, the effects of the use of low CN fuel on the performance of a LD single cylinder research engine operating in conventional and PCCI mode have been presented. Low CN blends were prepared by adding commercial gasoline or a low CN cyclic oxygenated compound (e.g. cyclohexanone) to a quality premium low sulphur diesel fuel. The oxygenated fuel is interesting because of its current availability and more suitable as PCCI-like fuel, and the latter because of its potential to be produced from lignin (i.e. second-generation biomass). Different mixtures with the two low CN fuels and diesel were prepared to obtain two blends with CN≈38 and two with CN≈20.

The present study has been focused to produce a detailed screening on the fuel effects on combustion and emission in the most important engine operating points for emission control, keeping the engine thermodynamic efficiency at the same current standards.

The experiments have led to several valuable results.

Use of low CN fuels in LD diesel engines

High premixing levels can be reached with low CN fuels, but combustion quality, in terms of stability, emissions and efficiency, is strongly affected by fuel characteristics (e.g. volatility, aromatics, and oxygen content).

In particular, it was evident that the use of low CN and volatile fuels (like gasoline), is very effective on the promotion of premixed combustion as well as over-mixing, and as consequence on UHC emissions. This effect becomes critical in those operating conditions where a pilot injection is required to control the combustion noise. Due to excessive over-mixing with very low CN fuels (e.g. CN≈20), the pilot activation becomes ineffective when its SOI is too early in the compression stroke. This is due to the low auto-ignition tendency of the CN20 blends and the low in-cylinder temperature. In this case, the adoption of a pilot close to the main injection or injection rate shaping could be useful to improve the trade-off of premixing time versus combustion noise and UHC emissions.

However, attributing the results to the tested combustion system design, low CN volatile fuels have limited EGR operating range with conventional injection strategies at low and medium load conditions. Moreover, as engine speed increase, fuels with greater auto-ignition resistance seem to become less tolerant to EGR.

A better compromise in terms of efficiency and emissions was found for blends at CN38, and so for limited fractions of both low CN fuels in diesel. In fact, also in full PCCI mode, aimed to push the engine towards very low NO_x emissions, the combustion became unstable for fuel blends at CN ≈ 20, while emission improvements at reasonable engine efficiencies were found for fuel blends at CN≈38.

Use of cyclic oxygenated fuels in LD diesel engines

The use of less volatile cyclic oxygenated fuels (better if renewable as CYCLOX) was found to improve the emissions at similar engine performance. In particular, where the diesel-gasoline blends give high PM and UHC emissions, the lower volatility and the oxygen content of the oxy-fuel limits the over-mixing phenomena and simultaneously reduce the soot formation rate.

This result was particularly pointed out when a pilot injection and high EGR rate were used in conjunction.

Similar results were attained in PCCI operating mode. In this case, in two of the four test points, acceptable working conditions were reached for the lowest CN blend of CYCLOX and diesel. However, the overall result analysis indicates that, also for CYCLOX, critical engine working conditions for emission and functionality can arise at very low CNs.

Moreover, as stated in paragraph 4.5, in the comparison between a high quality gasoline and a less volatile low CN oxy-fuel, as CYCLOX, an evidenced improvement of the engine stability, unburned and PM emissions at the same NO_x exhaust level can be obtained with the second one, for those engine operating conditions (e.g. transient, cold starting etc.) where a pilot combustion is required to the combustion control.

The present analysis underlines that in the continuous development of PCCI engines, the fuel properties play a fundamental role. To realize a more precise control of the in-cylinder air-fuel charge, before and during the combustion, future PCCI fuels have to be tailored to the desired combustion process. In this framework, renewable low CN oxygenated fuels could give a useful contribution.

Concerning the particle distribution, the use of low CN oxy-fuels as DC blend, evidences a general reduction of smoke emissions and of particle larger than 20-30nm. This aspect is interesting from a legislation point of view that will limit the number of emitted particles and larger than 23nm from 2014.

5 EXPERIMENTAL CHARACTERIZATION OF PCCI COMBUSTION VIA PFI INJECTION SYSTEM

5.1 Introduction

Although premixed combustion modes, in compression ignition engines, are studied as a promising solution to meet fuel economy and increasingly stringent emissions regulations, they are not still consolidated enough for practical applications. The high complexity of such combustion systems in terms of both air-fuel charge preparation and combustion process control requires, in addition to a deep experimental investigation, the employment of robust and reliable numerical tools to provide adequate comprehension of the phenomena.

As discussed in chapter 2 and 4, a precise control of auto-ignition time and heat release rate during combustion is necessary to extend engine operation under HCCI mode, avoiding misfire and knock risks, and to have high efficient combustions.

Therefore, in order to solve the HCCI control problems various investigation strategies can be applied also moving away from truly homogeneous mixtures, including PCCI combustion. One of the possible strategies is the use of more suitable fuels (HCCI-like fuels), i.e. low CN – oxy fuels, as described in chapter 4 or, as proposed in the present chapter, it is possible to premix the fuel or part of it in the intake manifold (HCCI – PFI). In this case, the "homogeneous" mixture is partially or fully created in the intake system allowing more time for premixed fuel evaporation and air mixing.

The possibility to operate the engine with two different fuel types (dual-fuel) at the same time is also under investigation and represents a combination between PCCI and HCCI combustion [104]. In this case, a high ON fuel is port-injected and a high CN fuel, which is directly injected into the cylinder, ignites the resulting air-fuel mixture. This allows a very precise control of the auto-ignition time and, by varying the premixed ratio, it is possible to cover a wide range of engine speed and loads. Several studies have revealed the advantages of dual fuel combustion

mode, showing a simultaneous reduction of NO_x and soot emissions, at the expense of CO and UHC increase [132][133].

For this reason, both numerical and experimental studies on the flame structure are important to identify how premixed charge auto-ignition and flame propagation are influenced by the ratio between the amount of premixed and direct-injected fuel.

The use of multi-dimensional models, supported by detailed chemistry, will probably allow a better explanation for experimental findings. Furthermore, CFD simulation will make possible to optimize the injection strategy and charge premixing levels for different operating points in a relatively short time [21].

Therefore, the aim of this test campaign was to employ a test procedure able to provide, additional experimental information in terms of capability of HCCI-PFI (port fuel injected fuel) in addition to HCCI-DI (direct injected fuel) combustion mode and, to develop and validate suitable numerical models evaluating the effects of charge premixing levels in Diesel combustion.

The tests were performed by varying the charge premixing level from the typical diesel combustion mode towards an almost completely premixed/HCCI mode using n-heptane as a direct injected fuel, and both n-heptane or ethanol as a port-injected fuel.

The use of such fuels (single component) allowed a detailed investigation of the "mixed injection conditions", that are typical of dual fuel configurations without employing fuels of different chemical nature, composition and ignition tendency.

Firstly, the choice of using a single fuel, n-heptane as DI and as PFI fuel, was motivated by the need to isolate the effects of different premixing levels and the resulting interaction between the charge and the fuel spray. Secondly, the use of n-heptane as DI injected fuel and ethanol (with low CN) as PFI fuel, was aimed to investigate on the possibility to realize (and to control) an equal combustion timing for the two fuels.

In order, to realize a homogeneous air-fuel charge, the intake manifold was modified to provide the desired extent of fuel port-injection (PFI). The port fuel injection system is described in paragraph 5.2.

5.2 Experimental setup

The experiments were conducted on the single cylinder engine widely described in Chapter 3. The "mixed injection conditions" (HCCI-PFI plus HCCI-DI) typical of dual-fuel configurations is realized through a fuel vaporizer containing a glow plug (Figure 5.1) able to vaporize the injected fuel. The nominal voltage of the glow plug is 14V and the maximum Power supply is about 300W. The glow plug temperature was settled at about 475K to guarantee the complete vaporization of the injected fuel.

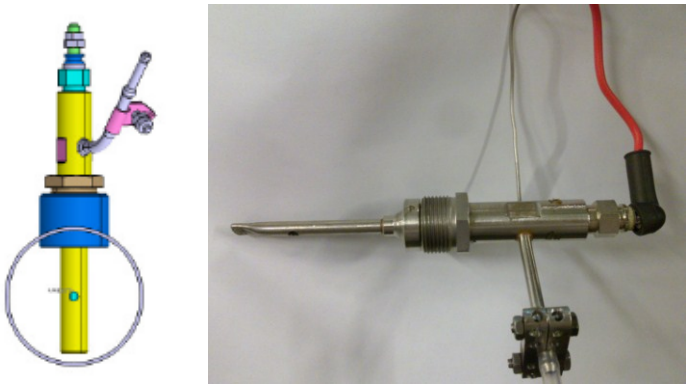


Figure 5.1: Vaporizer with integrated glow plug.

The vaporizer is placed just upstream the intake runners as evidenced in Figure 5.2. In order to avoid fuel deposits in the intake manifold the intake air is heated through electrical heater at about the same boiling temperature of the port-injected fuel (~375K).

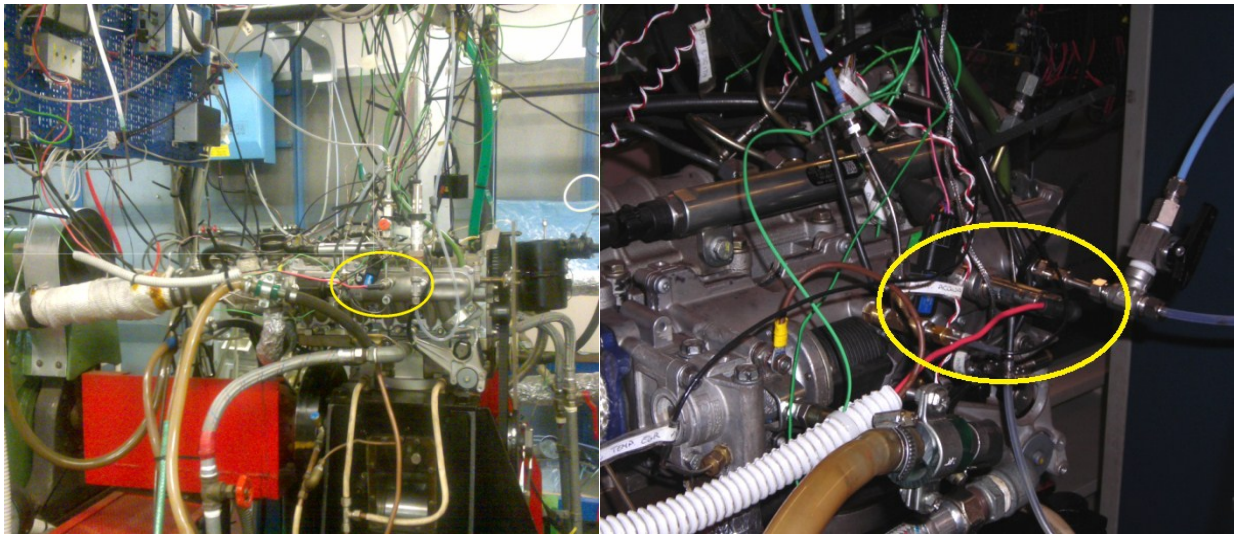


Figure 5.2: Vaporizer placed upstream the runners.

The control and the power unit of the vaporizer were realized in Istituto Motori (Figure 5.3). The control unit is able to regulate the fuel pump frequency and therefore the fuel mass flow rate delivered to the vaporizer. Moreover, the unit permits to manage the heating time of the glow plug.

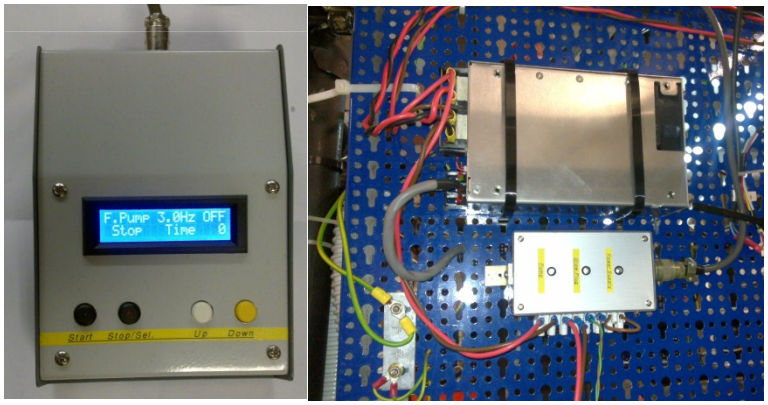


Figure 5.3: Control unit and power unit.

5.3 **Fuels**

As already stated, the choice of using n-heptane (n-$C_7H_{16,}$ single component fuel) for direct injection and for port fuel injection(or premixed) fuel derives from the need to isolate the effects

of different premixing levels and the resulting interaction between the charge and the fuel spray. N-heptane has a relatively low boiling point and excellent ignition ability (CN 56, equivalent to that of diesel fuel).

The use of ethanol as a PFI fuel was due to its low CN that permits to some extent a better control of the combustion phasing as described further.

The physical and chemical characteristics of the used fuels are reported in Table 6.1. Part of this table is reported in Table 5.1.

Feature	Method	**n-heptane**	**Ethanol**
Density @ 15 °C [kg/m3]	EN ISO 12185	684	790
Viscosity a 40 °C [mm2/s]	EN ISO 3104	0.51	1.01
Oxydation Thermal Stability a 110°C h	EN 14112	-	
Cetane Number	EN ISO 5165	56	<10
Low Heating Value [MJ/kg]	ASTM D3338	44	30
Distillation [°C]	IBP	98	78
°C	10% vol.	-	
°C	50% vol.	-	
°C	90% vol.	-	
°C	95% vol.	-	
°C	FBP	98	78
Carbon [molar%]	5991	83.9	52.2
Hydrogen [molar%]	5991	16.1	13.1
Nitrogen [molar%]]	5991	0	
Oxygen [molar%]	5991	0	34.7

Table 5.1: Main fuel properties.

5.4 Experimental procedure

In this work, the characteristics of premixed combustion mode and the effects of different premixed ratios were investigated. Different premixed ratios were obtained by adjusting the

quantities of premixed fuel (PFI) while keeping a fixed direct injected fuel (DI) quantity at a constant engine speed.

Starting from DI conditions, the premixed quantity is gradually increased rising the premixed ratio. Premixed combustion mode is characterized by a premixed ratio defined using the following equations:

$$r_{pm} = \frac{m_p}{m_p + m_d}; \quad (1) \qquad r_{pe} = \frac{m_p h_p}{m_p h_p + m_d h_d}; \quad (2)$$

where m_p and m_d indicate the mass flow rate of premixed fuel (PFI) and directly injected fuel (DI) respectively; whereas h_p and h_d are the lower heating values of the PFI and DI fuels. Equation (1) and (2) define the premixed ratio in terms of mass and energy respectively. Obviously if the DI fuel and PFI fuel are the same, the equation (1) and (2) coincide.

Thus, $r_p = 1.0$ is equivalent to fully HCCI and $r_p = 0$ means the conventional DI. ϕ indicates the total fuel equivalence ratio.

The tests were performed starting from the reference test points reported in Table 5.2.

Test point[15]	RPM [1/min]	IMEP [bar]	BMEP [bar]	MBF50% [CA]
1500x3(2)	1500	3.2	2	12
2000x7(5)	2000	6.9	5	15

Table 5.2: Reference points

Moreover, a direct injection (DI) strategy of one shot per cycle was adopted in order to discern the DI and PFI fuel effect on the combustion.

Starting from these operating conditions, a first set of experiments was performed in order to evaluate the influence of r_p on combustion process and engine performance at constant total fuel equivalence ratio or, at constant IMEP in the tests with using ethanol as PFI fuel. Therefore, maintaining the value of ϕ or IMEP, equal to the value of the reference starting point, PFI fuel was increased and DI fuel "proportionally" decreased.

[15] The values inside the parenthesis are referred to the BMEP value. The graphs that follows, sometimes refer to IMEP other times to BMEP(i.e. 1500x2 or 1500x3).

The second set of tests was addressed to investigate the effect of PFI fuel addiction on combustion evolution at fixed DI injected fuel mass. Different premixed ratios are obtained by increasing the quantities of PFI fuel while keeping intact the DI parameters (fuel mass, SOI and injection pressure). In this way test exhibits increased values of premixed ratio, and vary for MBF50%, IMEP and global fuel equivalence ratioϕ.

Temperatures of intake air, oil and coolant water were held stable during the experiments. As mentioned before, due to the need to isolate the effects of different factors on combustion, EGR was not applied in this experimental campaign.

As already, hint, the test were performed using n-heptane as DI fuel and n-heptane or ethanol as a PFI fuel:

- Case1: n-heptane (DI) – n-heptane (PFI)
- Case2: n-heptane (DI) – ethanol (PFI)

5.5 Results and discussion

5.5.1 Case1: n-heptane (DI) – n-heptane (PFI)

1500prm at fixed 3.2bar IMEP

The performed test points are summarized in Table 5.3. Moreover, the point 1500rpm@3bar IMEP (#1) correspond to the reference point reported in Table 5.2 and represent one of the most significant test point in terms of emissions computation(see Figure 4.2). Starting from these operating conditions, a first set of experiments was performed in order to evaluate the influence of r_p on combustion process and engine performance at constant total equivalence ratio. Therefore, maintaining the value of ϕ equal to the value in DI combustion (test #1), premixed combustion mode with a mixed PFI-DI injection (test #2, 3 and 4) and a fully homogeneous HCCI combustion with only PFI injection (test #5) were reproduced.

Test	Inj.	DI Fuel [kg/h]	PFI Fuel [kg/h]	r_p	Φ	IMEP [bar]
1	DI	0.4	0	0	0.28	3.2
2	PFI+DI	0.30	0.13	0.30	0.28	3.2
3	PFI+DI	0.23	0.19	0.46	0.28	3.2
4	PFI+DI	0.18	0.27	0.64	0.28	3.2
5	PFI	0	0.39	1.00	0.28	2.2

Table 5.3: Experimental engine test conditions with constant ϕ.

Figure 5.4 shows the pressure and heat release rate (RoHR) comparisons of different combustion ignitions: DI combustion (test #1, rp=0), premixed combustion (test #2, 3 and 4) and fully HCCI combustion (test #5) at ϕ equal to 0.28. It is worth to notice that, while tests from #1 to #4 produce the same value of IMEP, HCCI mode (test #5) presents a sensible reduction of the thermodynamic efficiency(Figure 5.5) and, as a consequence, a sensible reduction of the measured IMEP. HCCI combustion mode shows, as expected, higher peak pressure (Figure 5.4) and thermodynamic temperature (Figure 5.4, bottom right). As well-known curves of heat release rate (ROHR) show that test #3 is characterized by the expected two-stage combustion of fully HCCI conditions, while test #2, with a premixed ratio of 0.45, exhibits three-stage combustion. In agreement with many results [132], the combined HCCI-DI and HCCI-PFI combustion exhibits three-stage combustion. Curves of heat release rate evidences in fact a typical two-stage auto-ignition of n-heptane due to PFI fuel combustion and a third diffusive combustion due to the directly injected fuel (HCCI-DI). Heat release rate for HCCI combustion shows low temperature reactions (LTR) in the cool flame (NTC) region at about 800K and high temperature reactions (HTR) at about 1000K in agreement with [134].

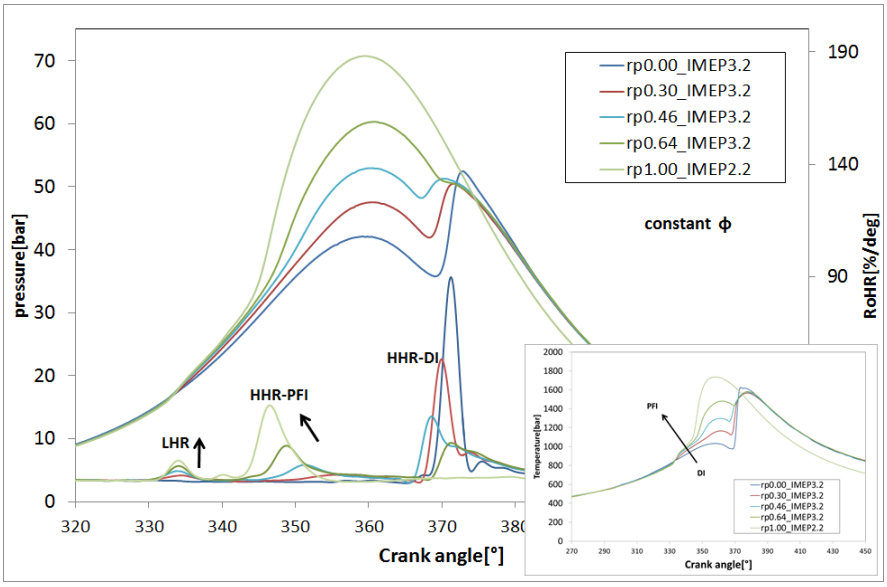


Figure 5.4: In-cylinder pressure, RoHR and thermodynamic bulk temperature (bottom right) evolution for the test cases with a fixed global fuel equivalence ratio with different levels of premixing charge.

In Figure 5.5 are reported the emission indices and efficiencies. In particular, the HC and CO emissions increase with increasing the premixing ratio (r_p) whereas the NOx decrease drastically. Conversely, in contradiction with the expected results, when the combustion become more premixed, albeit the smoke is at very low level (smoke•100), it increases. This could be explained by the following considerations:, more premixed become the combustion more the local temperature can be assumed equal to the bulk temperature; moreover, increasing r_p, the bulk combustion temperature increase at about 1800 - 1900K (Figure 5.4, bottom right). Therefore referring to the Kamimoto and Bae diagram(Figure 2.4) the local temperature in the case of higher r_p is lower than the NOx formation temperature but not out of the soot formation zone. Thus, probably in some regions of the in-cylinder charge, the local fuel-air ratio ϕ is at values in the low soot formation area. Analogous results are stated in [132] where the higher local ϕ are justified with the fact that higher is the fuel (n-heptane) injected in PFI conditions, less is the in-cylinder oxygen concentration therefore the premixed charge play a similar role as EGR, when the DI combustion start. Furthermore, the boundary regions of the DI fuel spray are at higher pressure and temperatures causing a poorer evaporation of the fuel core of the spray favouring the soot formation. For r_p=1 this considerations are less valid and probably, the not expected higher soot is caused by a poorer evaporation of the high quantity of PFI fuel causing

fuel rich regions inside the cylinder; besides the lower combustion temperature does not permit the complete oxidation of the formed soot.

The decrease of the fuel efficiency is due to the increase of CO and HC emissions increasing the premixed ratio (Figure 5.4) but, also to the difficulty to control the combustion phasing mainly in fully PFI condition(r_p=1). In fact, Figure 5.6 shows the even more delayed start of injection (SOI) of the direct injection (DI) as the premixed ratio increase in order to keep constant the thermodynamic efficiency and at the same level of the DI case. In fully PFI condition, due to the high auto-ignition tendency of n-heptane the combustion is advanced to values before top dead center(TDC) (Figure 5.6) lowering the thermodynamic and thus the fuel efficiency[16] (Figure 5.4).

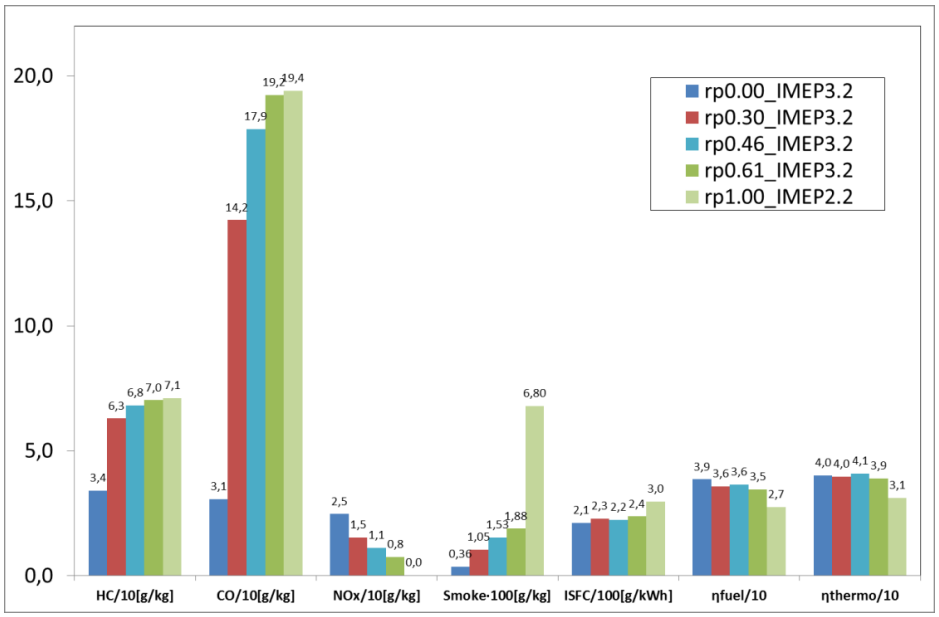


Figure 5.5: Emission indices and efficiencies for the test cases with a fixed global fuel equivalence ratio (Φ=0.28) with different levels of premixing charge.

[16] See the definitions of the efficiencies in Appendix B.

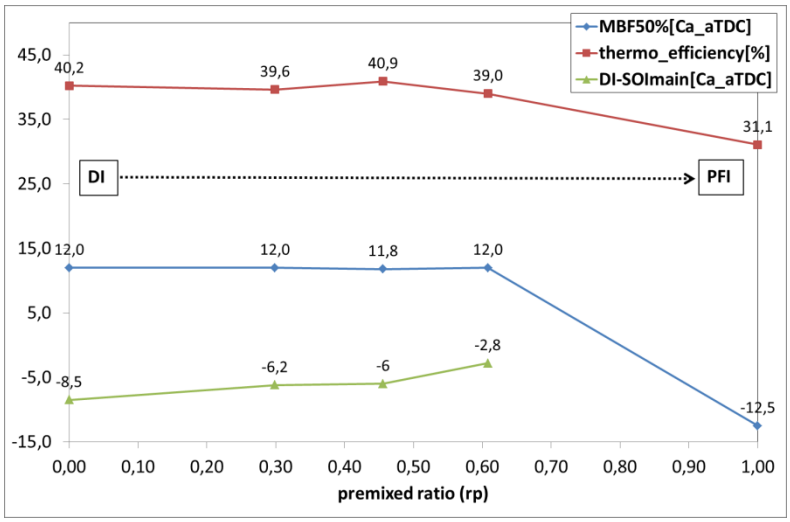


Figure 5.6: MBF50%, thermodynamic efficiency and SOI-DI as a function of premixed ratio (rp) at constant Φ.

1500prm at fixed DI (3.2bar) and adding PFI

The second set of tests was addressed to investigate the effect of PFI fuel addiction on combustion evolution of a fixed DI injected fuel mass (test #1, Table 5.4). Engine tests from #2 to #4 were performed with different premixed ratios obtained by increasing the quantities of PFI fuel while keeping intact the DI parameters (fuel mass, SOI and injection pressure). In this way test points from #2 to #4 exhibits increased values of premixed ratio, and vary for MBF50%, IMEP and global fuel equivalence ratioϕ. Moreover, the load was limited at 5.8bar of IMEP because knocking occurs for higher loads.

Test	Inj.	DI Fuel [kg/h]	PFI Fuel [kg/h]	r_p	Φ	IMEP [bar]
1	DI	0.4	0	0	0.28	3.2
2	PFI+DI	0.4	0.1	0.19	0.35	4.0
3	PFI+DI	0.4	0.2	0.34	0.43	4.8
4	PFI+DI	0.4	0.4	0.45	0.5	5.8

Table 5.4: Experimental engine test conditions with constant DI and increasing ϕ.

Curves of Figure 5.7 summarize results relative to the effect of partial premixing. The premixed ratio was increased and the total fuel mass was increased through the addiction of PFI n-heptane to a fixed in-bowl injected fuel mass.

In agreement with literature [132], experimental results show that, without EGR; the ignition timing of low temperature cool flame is poorly influenced by the variation of r_p and Φ, and occurs at about 35° BTDC. On the contrary, with the rise of r_p, the second stage of combustion (HHR-PFI) advances significantly and shows progressive heat release increment of HCCI combustion. In addition, the peak values of cylinder pressure increase with the increase of premixed ratio.

Considering the combustion of the direct injected fuel mass, the third peak of heat release rate is typical of a diffusive combustion. When r_p is increased from 0 (test #1) to 0.25 (test #4), the maximum peak of RoHR of DI conditions is significantly reduced, due to a sensible reduction of ignition delay time of the DI fuel. As evidenced in the Figure 5.7, the phasing of diffusive combustion of the DI fuel is not influenced by a further increase of r_p. Ma *et al*. [132] attribute this behaviour to a resulted minimal diffusive ignition delay time deriving from high in-cylinder temperature and pressure conditions produced by HCCI combustion. With respect to such interpretation, it is worth to precise that such result depends on the strong reduction of the chemical ignition delay of the DI fuel so the physical ignition delay becomes the controlling factor of diffusive combustion.

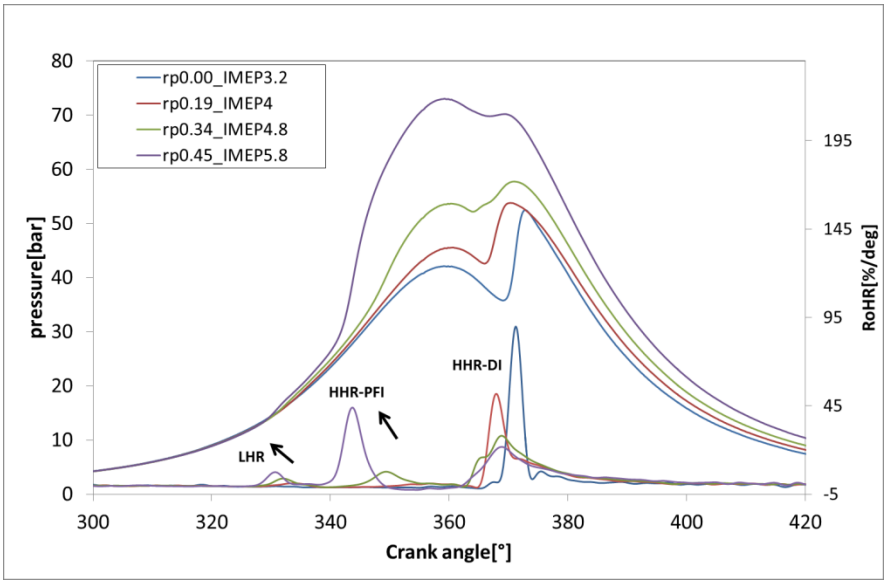


Figure 5.7: In-cylinder pressure and RoHR evolution at 1500rpm with variable global fuel equivalence ratio and different levels of premixing charge.

In Figure 5.8, the emission indices and efficiencies are reported. In particular, for the test points from #1 to #3 the HC, CO and smoke emissions increases and the NOx decrease. Such trends are in agreement with the results at constant ϕ and due to the combined effect of PFI injection and charge premixing. The efficiencies are more or less as the DI one.

The emissions of test #4 show a trend inversion. In particular, the HC, CO and smoke emissions are lower compared to the previous cases due to the higher in-cylinder temperatures (higher load) that oxidize HC and smoke and permit a more complete conversion of CO to CO_2.

As for the previous cases, the decrease of fuel efficiency is attributable to the difficulty to control the combustion phasing. In fact, pressure and RoHR traces (Figure 5.7) show an advance in combustion timing, away from the optimum value, leading to a lower thermodynamic efficiency[17] (Figure 5.8).

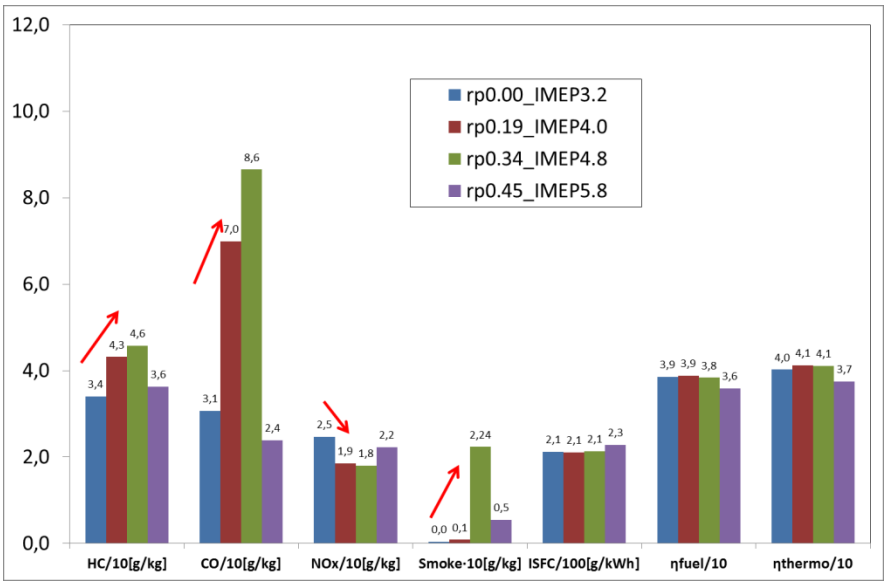


Figure 5.8: Emission indices and efficiencies at 1500rpm with variable global fuel equivalence ratio for different premixing ratio.

The experimental results were provided for the calibration of the combustion model using OpenFoam as numerical tool. Figure 5.9 reports the evolutions of chemical species produced during the combustion and computed after the calibration.[21].

[17] See the definitions of efficiencies in Appendix B.

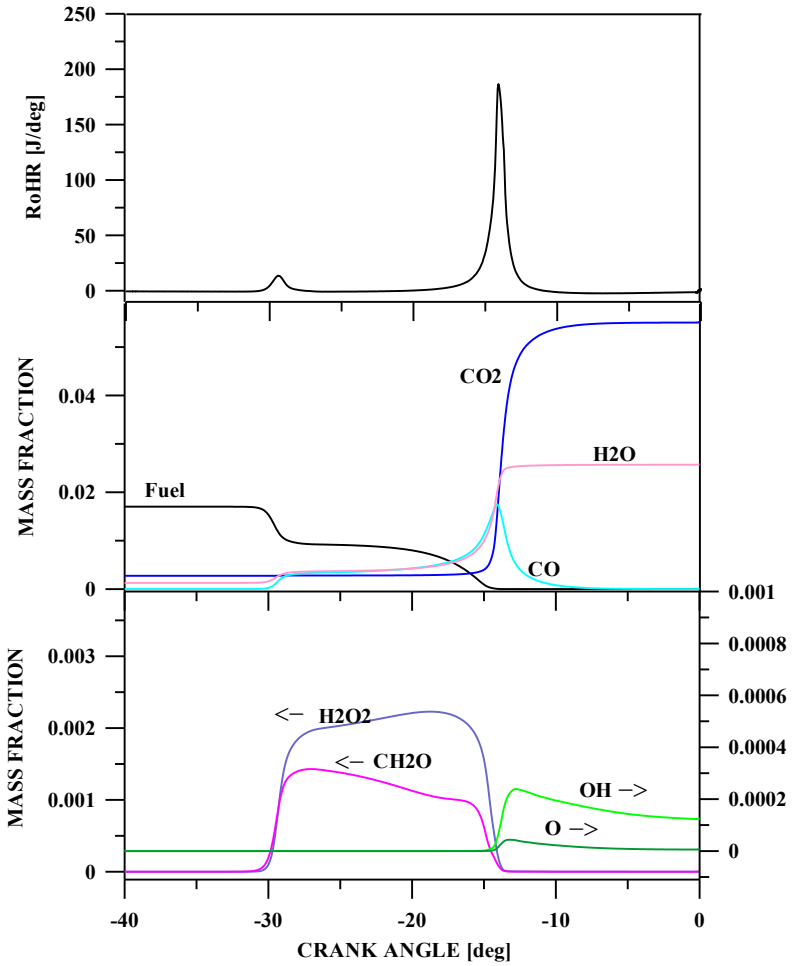


Figure 5.9: Computed histories of significant chemical species and the corresponding RoHR for case #4 (PFI+DI) IMEP 5.8bar.

Looking at the histories of significant chemical species in case #4 (Table 5.4), together with the corresponding RoHR, it is possible to follow the ignition phenomena of the premixed fuel fraction. The first RoHR peak, corresponding to the first reduction in the fuel concentration, is characterized by a typical low temperature dynamics, as fuel consumption corresponds to a marked formaldehyde increase and the hydrogen peroxide accumulation. Moreover, a first step of carbon monoxide increment takes place, as visible from the respective profile at 30 CAD BTDC. At about 15 CAD BTDC the hydrogen peroxide decomposition, linked to the high temperature branching event, determines the second stage of ignition, with the consequent OH radicals release, the carbon monoxide oxidation and the complete fuel consumption. It is interesting to notice that the high temperatures reached in this second event allow the survival of

a certain amount of OH and O radicals, that, starting from 10 CAD BTDC, keep to decrease quite gently: it follows that the subsequent directly injected fuel not only is admitted in a very hot environment, but it is also set next to these active radicals, capable of greatly enhance its ignition.

This is an example of how, the development of suitable numerical and reliable tools are fundamental to provide additional information for an adequate comprehension of the complex combustion phenomena of PCCI.

5.5.2 Case2: n-heptane (DI) – ethanol (PFI)

In this set of experiments, n-heptane is used as a direct injected fuel whereas ethanol is used as port injected fuel. The use of ethanol as a PFI fuel derives from the possibility to use both a low boiling fuel and an oxygenate renewable fuel. Moreover, ethanol has a very low CN that permits to some extent a better control of the combustion phasing as described further.

The test procedure is similar to that used for the test with n-heptane. Different premixed ratios were adopted by varying "proportionally" the quantities of DI and premixed fuel. In particular, at constant IMEP varying the premixed ratio (varying the quantities of DI and PFI fuel) and at constant DI fuel increasing the PFI fuel. These procedures are adopted starting from both the reference points reported in Table 5.2. It is worth to note that since the DI and PFI fuels have different energy content, the premixed ratio is defined in energy terms r_{pe}[18] (see equation (2), paragraph 5.3). In fact, the energy content of ethanol at the same injected mass is much lower than that of n-heptane. This is confirmed by Figure 5.10 that shows the correlation between r_p and r_{pe}. The lower LHV[19] of ethanol (Table 5.1) lead to a higher injected mass compared to n-heptane if certain energy is desired.

[18] Using different fuels for DI and PFI injection it is preferable refer to the premixed ration in energy terms, see equation (2).
[19] Low heating value.

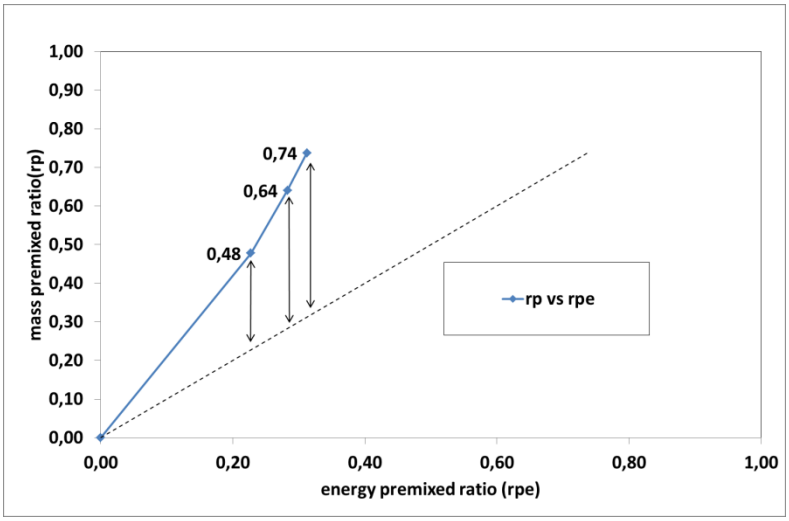


Figure 5.10: Correlation between rp and rpe using n-heptane as DI fuel and ethanol as PFI fuel.

1500prm at fixed 3.2bar IMEP

The test points are summarized in Table 5.5. Moreover, the first test point, IMEP (#1) corresponds to the reference point reported in Table 5.2. Starting from this point, the premixed combustion was realized varying the DI and PFI fuels (test #2, 3 and 4) maintaining the IMEP constant and equal to the value in DI combustion (test #1). Obviously it was not possible to perform the fully HCCI with only ethanol.

Test	Inj.	DI Fuel [kg/h]	PFI Fuel [kg/h]	r_{pe}	IMEP [bar]
1	DI	0.39	0	0	3.2
2	PFI+DI	0.29	0.27	0.23	3.2
3	PFI+DI	0.21	0.39	0.28	3.2
4	PFI+DI	0.17	0.49	0.31	3.2

Table 5.5: Experimental engine test conditions at constant IMEP.

Figure 5.11 shows the pressure and heat release rate (RoHR) comparisons of different combustion ignitions: DI combustion (test #1, r_{pe}=0) and premixed combustion (test #2, 3 and 4). In this case is not present the characteristic two-stage heat release of the premixed combustions noted in the case of n-heptane as PFI fuel. The reason is the low auto-ignition tendency (low CN) of ethanol that does not exhibits the low temperature heat release. Curves of

heat release rate evidence in fact that, the combustion of the premixed charge starts when the DI fuel auto-ignite. This allows a better control of the combustion phasing that is one of the challenges of the HCCI application (see paragraph 2.2.5).

Increasing the premixed ratio, only a slight variation of the DI-SOI (direct start of injection) is needed (Figure 5.13) to phase the combustion, and this evidence again the easier control of the combustion using, as PFI, low CN fuels. The control of the combustion permits the keep almost constant the thermodynamic efficiency (Figure 5.12, Figure 5.13). Therefore, the lower fuel efficiencies for higher premixing ratios are linked only to the lower combustion efficiency (higher CO and HC, thus ISFC). In fact, Figure 5.12 shows the expected higher CO and HC increasing the premixed ratio.

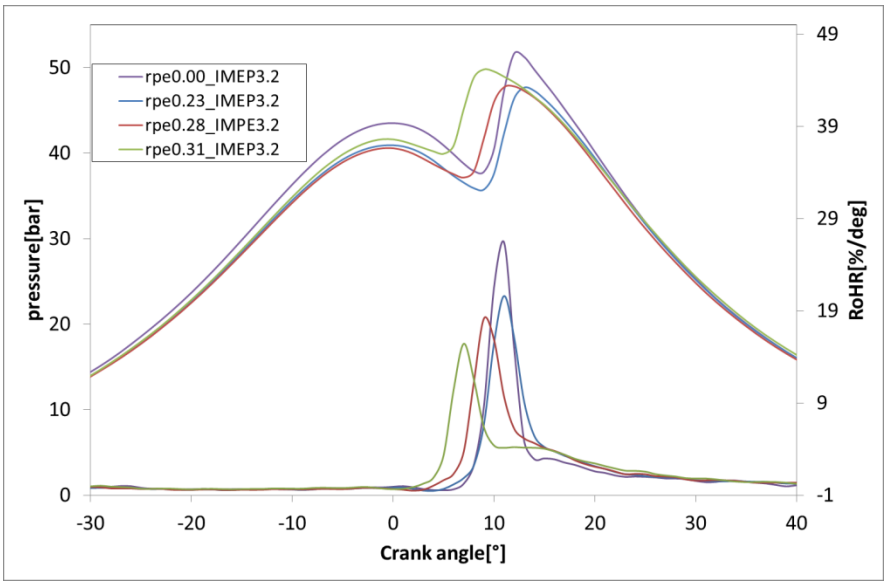


Figure 5.11: In-cylinder pressure and RoHR evolution at 1500x3.2 varying the global fuel equivalence ratio and for different premixing ratio.

Moreover, compared to Figure 5.5, where n-heptane was used as PFI fuel, the soot emission decreases drastically. This can be recognized to the better mixing process (low CN-more time available) and to the presence of intra-molecular oxygen of ethanol. In addition, the NOx emission decreases, in some measure and increasing the premixed ratio. Probably for higher premixing ratios, the NOx could be lower but in the performed tests, the mixing ratio was limit at 0.23 due to the increase of combustion instability (COV~6.5, Figure 5.13).

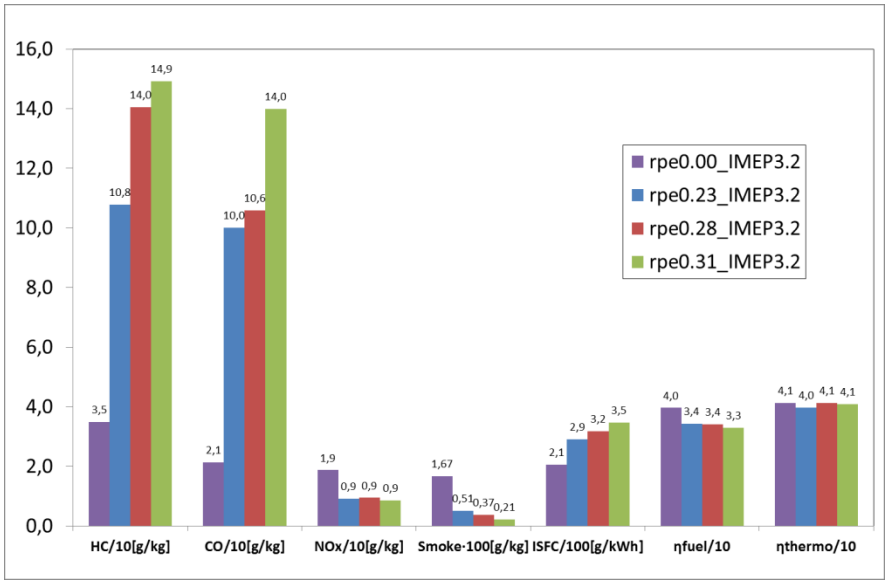


Figure 5.12: Emission indices and efficiencies for the test cases with a fixed IMEP=3.2bar for different levels of premixing charge.

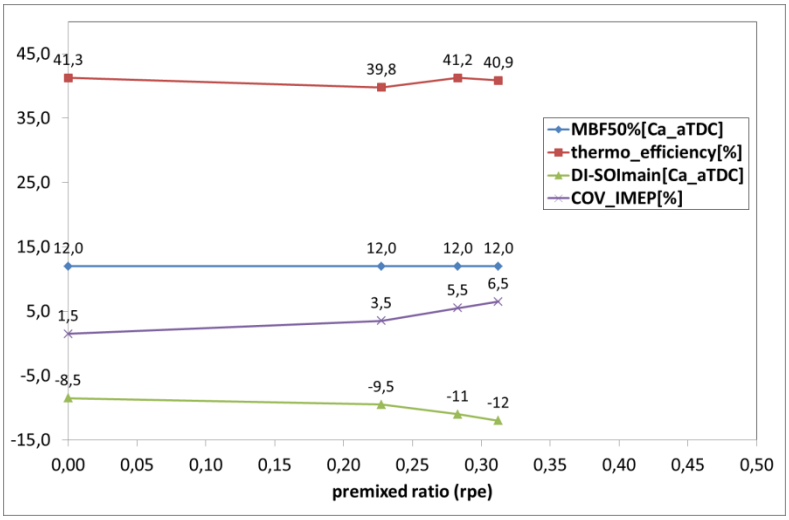


Figure 5.13: MBF50%, thermodynamic efficiency, COV and SOI-DI as a function of premixed ratio rp, at 1500rpmx3.2bar IMEP.

1500prm at fixed DI (3.2bar) and adding PFI

The second set of test, in the same way as with n-heptane, was addressed to investigate the effect of PFI fuel addiction on combustion evolution at fixed DI injected fuel mass. Different premixed ratios were obtained by increasing the quantities of PFI fuel while keeping intact the DI parameters (fuel mass, SOI and injection pressure). In this way test exhibits increased values of premixed ratio and IMEP. In particular the test point are summarized in Table 5.6

Test	Inj.	DI Fuel [kg/h]	PFI Fuel [kg/h]	r_{pe}	IMEP [bar]
1	DI	0.39	0	0	3.2
2	PFI+DI	0.39	0.16	0.15	4.0
3	PFI+DI	0.39	0.29	0.21	4.8
4	PFI+DI	0.39	0.45	0.25	5.8
5	PFI+DI	0.39	0.77	0.29	7.7

Table 5.6: Experimental engine test conditions at constant DI increasing PFI.

Figure 5.14 show the pressure traces, RoHR, emission and efficiencies. The RoHR show that also increasing the PFI fuel, the combustion is phased with the DI combustion. Thus, in the case of low CN fuels it is possible to control the combustion phase and then the thermodynamic efficiency for higher loads. Again, the premixed energy ratio was limited by the increase of the combustion instability (COV_IMEP) that reached values close to 10%.

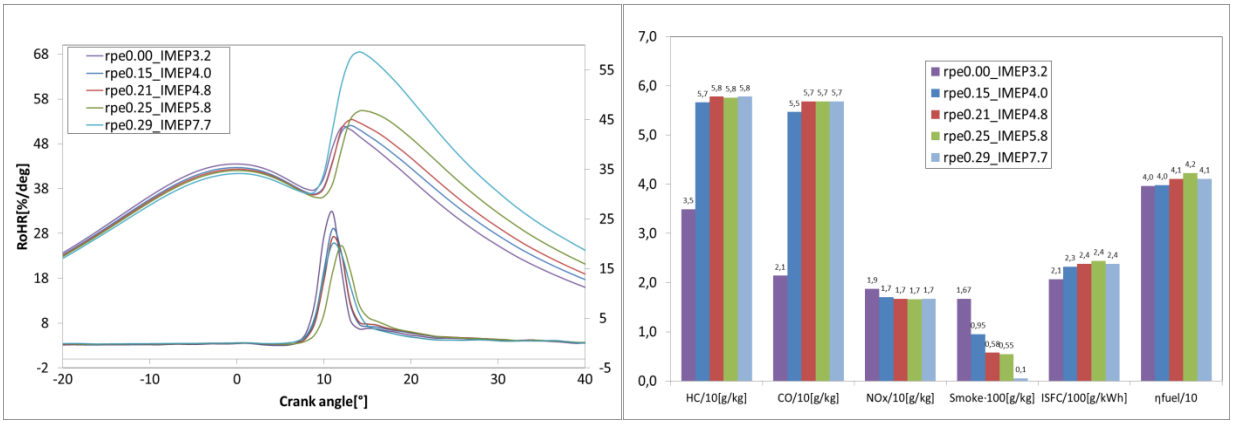


Figure 5.14: Pressure, RoHR, emissions and efficiencies at constant DI and increasing PFI.

Starting from the reference point at 3.2 bar IMEP, the HC and CO indices increase and the NOx decrease as r_{pe} goes from 0 to 0.15. Then the ratio remains constant also for further increases of the PFI fuel quantity. An important result is that at the same level of NOx, increasing the proportion of ethanol the smoke decrease even more. Therefore, the oxygen effect (or r_{pe} effect) is evident in terms of smoke reduction without penalizing other emissions or the efficiencies.

2000prm at fixed 6.9bar IMEP

Figure 5.15 shows again that HC and CO increase as the premixed ratio increase but this time NOx and smoke are clearly reduced without significant penalties in terms of fuel efficiency. Therefore, the premixing and the oxygen effect are evident.

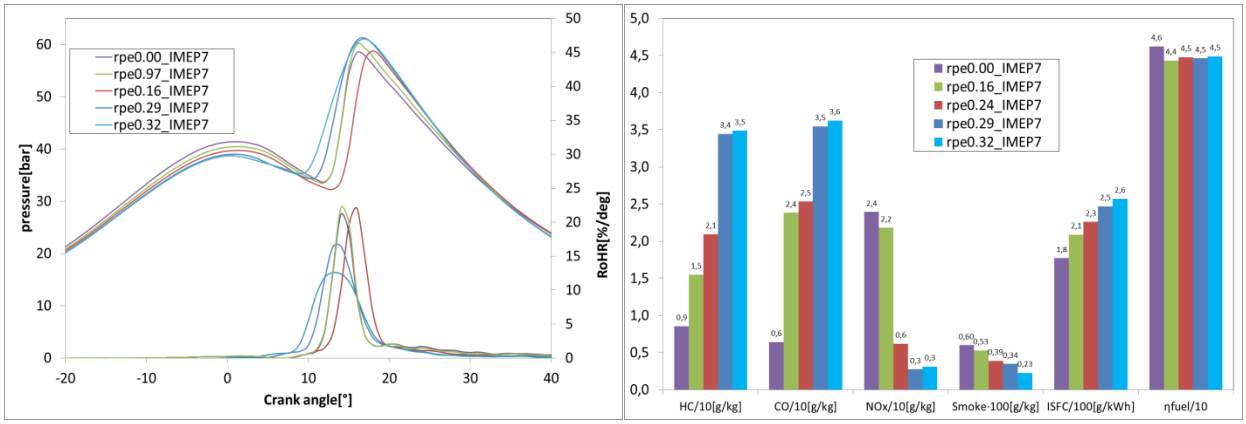


Figure 5.15: Pressure traces, RoHR emissions and efficiencies at 2000x6.9 at constant IMEP for different levels of premixing ratio.

Thus, it can be stated that also for higher speeds, it is possible to control the combustion phase with the use of ethanol as PFI fuel. The maximum COV was inside acceptable limits for the highest premixed ratio (~3.5).

2000prm pilot-main injection strategy at higher loads

The pilot plus main strategies was used to assess the effect of the pilot injection on the controllability of the combustion. Table 5.7 show the settings of the performed points.

Test	Inj.	DI Fuel [kg/h]	PFI Fuel [kg/h]	r_{pe}	SOImain [Ca aTDC]	MBF50% [Ca aTDC]	IMEP [bar]
1	DI	1.15	0.00	0.00	-7.5	15	7.8
2	PFI+DI	0.99	0.27	0.12	-6.7	15	7.8
3	DI	1.30	0.00	0.00	-7.5	15	8.3
4	PFI+DI	1.40	0.40	0.15	-4.7	15	8.3

Table 5.7: Experimental engine test conditions pilot-main injection strategy.

Therefore, in Figure 5.16 are compared DI and DI+PFI strategies using a pilot plus main injection for the direct injection. The continuous traces are referred to the DI+PFI injection whereas the dashed traces refer to the DI. In the case of PFI (continuous traces), the start of pilot injection is slightly delayed and this is probably due to the presence of ethanol in the intake charge that perhaps reduce the pilot efficiency. Again, thanks to the low auto-ignition tendency of the ethanol it was possible to settle the MBF50% to 15° Ca aTDC. Comparing the SOI values of DI+PFI and DI combustion modes, it is possible to state that, even if the pilot combustion is slightly delayed, part of the ethanol starts to burn before the DI - heat release occurs. Therefore, the MBF50% without any adapting of the SOI, would advance. Thus, the presence of pilot injection tends to advance the combustion phasing. This is an interesting result in terms of combustion control that is one of the challenges of the premixed combustion.

Therefore, a deeper investigation with a parametric test procedure is necessary to find an optimal combination in terms of timing and phasing of the pilot injection. Such approach could be useful for additional information in terms of combustion control.

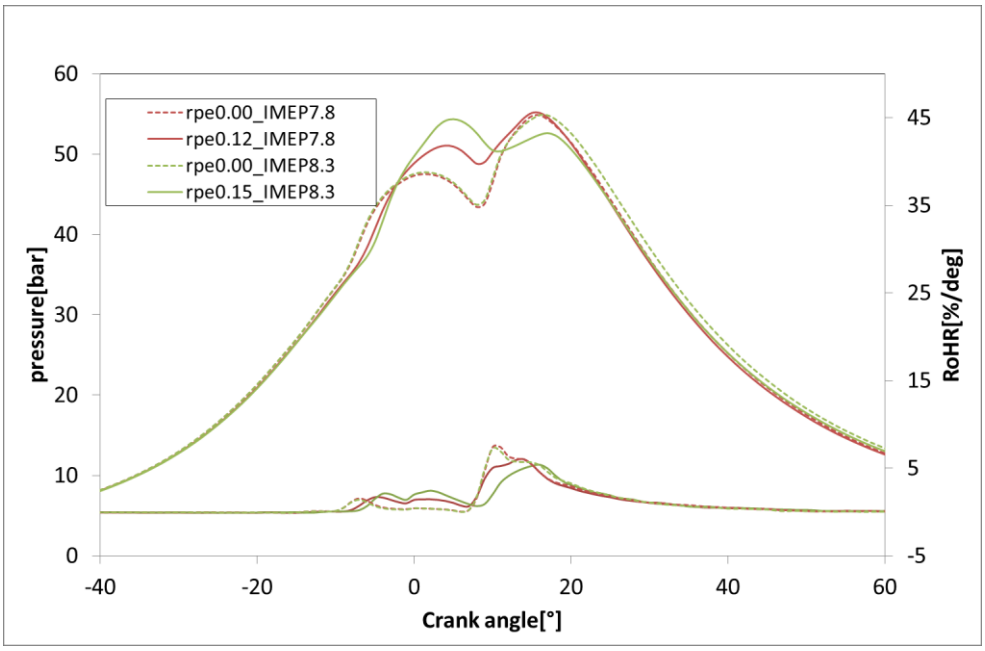


Figure 5.16: In-cylinder pressure and RoHR comparison at 2000x7.8 and 2000x8.3 with and without PFI.

However, both the lower efficiency of the pilot and the more premixed combustion lead to higher HC, CO and smoke emissions. A slight decrease in terms of NOx is shown increasing the premixed ratio compared to the DI conditions (Figure 5.17).

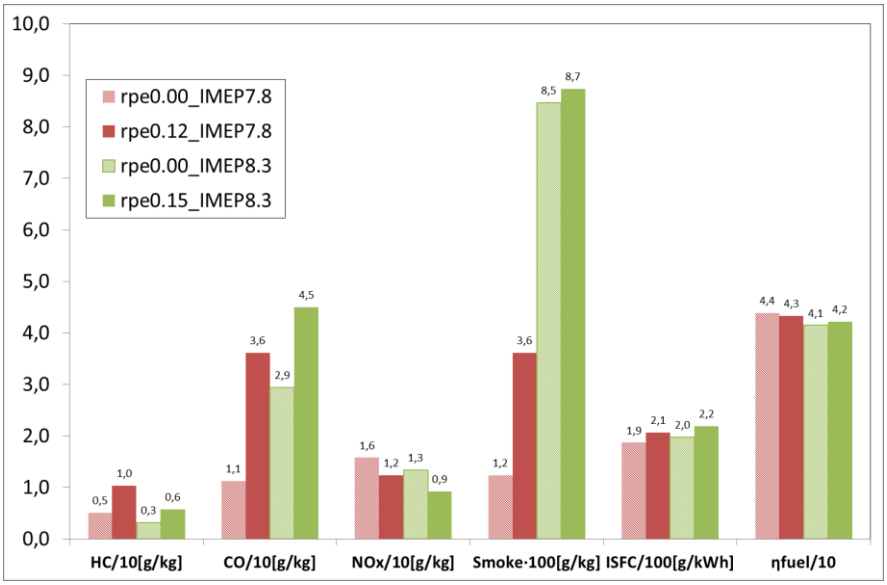


Figure 5.17: Emission indices and efficiencies comparison at 2000x7.8 and 2000x8.3 with and without PFI.

5.6 Nanoparticle emission from PFI-DI combustion

As already done in the previous chapter 4, measurements in terms of particle size distribution were performed at 1500rpm 3.2bar IMEP using ethanol as PFI fuel and varying the premixed ratio at constant IMEP. The results show similar trends as depicted in paragraph 4.7 for the DC blend that is also a low CN oxy-fuel like ethanol. The main engine parameters of this test are reported in Table 5.3.

Figure 5.18shows the PSDF (particle size distribution function measured at different premixed ratios.

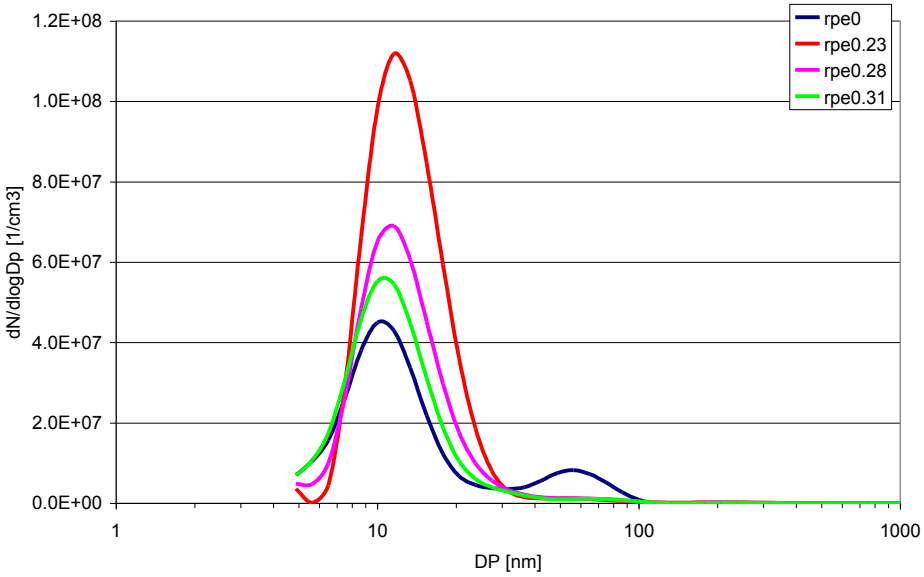


Figure 5.18: Particle size distribution measured at different premixed ratios.

The number of particles larger than 20nm strongly decreases when the port-HCCI was performed. On the other hand, the nuclei mode decreases at the increasing of the premixed ratio (rp) even if it remains higher with respect to the direct injection case. The better mixing and the higher oxygen content of ethanol mainly contribute to the lower emissions of large particles. Moreover, at the increasing of the rp the local in-cylinder temperature increases then the nuclei particle concentration decreases.

5.7 Conclusions

In the case of mixed combustion strategy, i.e. HCCI-DI and HCCI-PFI, the homogeneous mixture is partially created in the intake system allowing more time for premixed fuel evaporation and air mixing prior the auto-ignition through piston compression occurs. However, mainly using low boiling fuels, an effective premixed charge can be formed. On the other hand, high CN and low volatile fuels show limited premixing effects due their poor vaporizing tendency. In fact, problems due to wall wetting can occur. In particular, the liquid fuel can enter in to combustion chamber and can deposit on cylinder with a consequent increase of soot formation or can cause the dilution of lube oil.

Therefore, the aim of this test campaign has to have a screening of the PFI impact on the HCCI mixed combustion mode (DI+PFI).

Concerning the NOx emissions, it is possible to state that, premixing by port fuel injection has a positive effect on NOx reduction for both, n-heptane and ethanol as PFI fuel. This trend derives from the reduction of the local in-cylinder temperature because of an improved mixing process.

Concerning the soot emissions, different trends are observed. In the case of low boiling fuels with high CN (n-heptane), the high auto-ignition tendency does not permit the formation of a complete homogeneous charge. In fact, in the case of three-stage heat release, when the two stage combustion occurs before the diffusive combustion (presence of DI injection), the oxygen reduction and the higher pressures in the out-layer of the fuel spray lead to a poorer evaporation of the fuel core. For higher loads, there are some evidences that, the smoke emissions reduce due probably to the high in-cylinder temperature that permits a better soot oxidation of the DI rich zones.

In the case of using ethanol, different trends are observed. The soot emissions are reduced at any speeds and loads due to a combined factor of CN and oxygen effect. The lower CN permit an improved mixing process therefore the local equivalence ratio tend to shift the operating region out of the soot and NOx formation areas.

Concerning the combustion control, in the case of n-heptane as PFI fuel, due to its high auto-ignition tendency, an excessively and uncontrolled advance in auto-ignition of the premixed

charge are evidenced leading to a lower thermodynamic efficiency. Moreover, due to uncontrolled self-ignition, knocking may occur at higher loads. Therefore, for both reasons, the operating range was limited to lower loads.

The ethanol instead, thanks to its low CN, allows a very precise control of the auto-ignition time and, by varying the premixed ratio, it is possible to cover a wide range of engine speeds and loads In fact, in the performed tests, any significant advance of the main heat release can be noted therefore the thermodynamic efficiency remain constant.

Besides, a multiple injection strategy appears to be beneficial in terms of start of combustion control even if a deeper investigation is necessary to optimize the quantities and the phasing of the injections to avoid excessive emission and efficiency penalties.

Concerning the particle distribution, using ethanol as PFI fuel, the particles larger than 23nm tend to decrease as with DC blend. This could be an advantage to meet the future limits in terms of number of particles number.

6 SUMMARY

The present study has focused to produce a detailed screening on the benefits and drawbacks on the use of innovative fuels (as low CN oxy-fuels) and alternative fuel injection systems (as the PFI technology) for the application of advanced combustion concepts as HCCI and PCCI.
The experimental activity was limited to several engine operating conditions but adequate for an overall screening of the engine response in the working area subject to emission regulation.
A final summary of the research is reported in the following.
As general result, the oxygenated renewable fuels such as cyclic-oxygenated and ethanol are suitable as PCCI-like fuel, taking also into account that their production chain seems mature for medium/large scale application.
In the case of use low CN fuels in blend with diesel, high premixing levels can be reached but combustion quality, in terms of stability, emissions and efficiency, is strongly affected by fuel characteristics (e.g. volatility, aromatics, and oxygen content). In particular, it was evident that the use of low CN and volatile fuels is very effective on the promotion of premixed combustion as well as over-mixing, and as consequence on UHC emissions. This effect becomes critical in those operating conditions where a pilot injection is required to control the combustion noise, thus in the case of conventional injection strategy. Moreover, the lower volatility and the oxygen content of the oxygenated fuel limits the over-mixing phenomena and simultaneously reduce the soot formation rate. This result was particularly evidenced when a pilot injection and high EGR rate were used in conjunction.
However, the overall result analysis indicates that critical engine working conditions for emission and functionality can arise at very low CNs.

In the case of mixed combustion systems, i.e. DI-PFI, the homogeneous mixture is partially created in the intake system allowing more time for premixed fuel evaporation and air mixing prior the auto-ignition through piston compression occurs.

It was observed that mixed injection has a positive effect on NOx. This trend derives from the reduction of the local in-cylinder temperature because of an improved mixing process.
Contrarily, different trends for soot emissions were observed. High CN number fuels increase the soot emissions due their difficulties to realize well-premixed charges also using a PFI injection. In the case of low CN oxy-fuel (such as ethanol), the soot emissions are reduced at any speeds and loads due to combined factor of CN and oxygen effect.
Concerning the combustion control, low CN fuels allows a combustion overlapping of both the PFI and DI fuel charge. This permits, in principle, a precise control of the auto-ignition time and, by varying the premixed ratio, it is possible to cover a wide range of engine speeds and loads.
Besides, a multiple injection strategy appears to be beneficial in terms of start of combustion control even if a deeper investigation is necessary to optimize timing and phasing of the injections to avoid excessive efficiency penalties.

In conclusion, the present analysis underlines that in the continuous development of PCCI engines, the fuel properties and fuelling systems will play a fundamental role. To realize a more precise control of the in-cylinder air-fuel charge, before and during the combustion, future fuels and engine architectures have to be tailored to the desired combustion process.

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Appendix A

Feature	Method	**Petroleum diesel**	**GTL**	**RME**	**SME**	**n-heptane**	**Gasoline**	**Cyclo-hexanone**	**Ethanol**
Density @ 15 °C [kg/m3]	EN ISO 12185	840	777.5	883	884.4	684	720	950	790
Viscosity a 40 °C [mm2/s]	EN ISO 3104	3.141	2.547	4.254	3.958	0.51	0.5-0.75	4.9	1.01
Oxydation Thermal Stability a 110°C h	EN 14112	-	-	8.6	7.9	-	-	-	
Cetane Number	EN ISO 5165	56	73.9	52.3	48	56	~10	~10	<10
Low Heating Value [MJ/kg]	ASTM D3338	42.5	43.53	37.35	37.25	44	43	35	30
Distillation [°C]	IBP		203.1	322	320	98	-	155	78
°C	10% vol.		230.3	333.2	332.1	-	45	-	
°C	50% vol.	280.1	265.9	337	335	-	105	-	
°C	90% vol.	338.1	305.8	343.3	341.2	-	155	-	
°C	95% vol.		312.2	347	345.6	-		-	
°C	FBP	362	317.3	360	362	98	190	155	78
Carbon [molar%]	5991	86.5	84.3	78.5	78.4	83.9	85-88	73.4	52.2
Hydrogen [molar%]	5991	13.5	14.4	10.8	11.0	16.1	12-15	10.3	13.1
Nitrogen [molar%]]	5991	-	1.3	0.2	0.2	0			
Oxygen [molar%]	5991	-	0.0	10.5	10.4	0	0	16.3	34.7

Table 6.1: Fuel properties

Appendix B

Combustion efficiency

$$\eta_{comb} = \frac{Q_{out}}{Q_{in}} = \frac{Q_{in} - Q_{lost}}{Q_{in}} = 1 - \frac{Q_{lost}}{Q_{in}}$$

Thermodynamic efficiency

$$\eta_{thermo} = \frac{\eta_{fuel}}{\eta_{comb}} = \frac{1}{ISFC \cdot LHV_{fuel} \cdot \eta_{comb}}$$

Indicated specific fuel consumption

$$ISFC = \frac{\dot{m}_{fuel}}{P_{ind}}$$

Kay's mixing rule with x_i the mole fraction

$$CN_{mix} = \sum x_i CN_i$$